**CR 93.007** 

# NCEL

**Contract Report** 

September 1993

An Investigation Conducted by Arthur D. Little, Inc. Cambridge, MA

# TEST AND EVALUATION OF A PILOT SYSTEM FOR ION EXCHANGE TREATMENT OF CADMIUM CYANIDE WASTES

Abstract Developmental tests were conducted for an ion exchange process developed to treat rinsewaters generated from cadmium cyanide electroplating operations. Results of previous laboratory studies were used as the basis of design for the construction of a pilot-scale system that was installed at the North Island Naval Aviation Depot, San Diego, CA. In this process, a chelating cationic resin in the sodium form is used to remove Cd<sup>+2</sup> followed by a strong base anionic resin for removal of free cyanide. Tests were conducted using both simulated rinsewaters and actual wastewaters. The results showed that the removal of Cd+2 was successful in all cases and the effluent concentration was below the Federal Pretreatment Standards in most cases. The success of the cation resin is due to its ability to break the metal cyanide complex and selectively remove Cd<sup>+2</sup> even in the presence of high concentrations of other cations. The removal of CN was not as successful. Effluent concentrations were above Federal discharge standards. The cationic resin was regenerated with sulfuric acid, producing a concentrated solution of cadmium sulfate. Cadmium was recovered from the regenerant solution by electrowinning. The anionic resin was regenerated with sodium hydroxide, producing a concentrated sodium cyanide solution.



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Developmental tests were conducted for an ion exchange process developed to treat rinsewaters generated from cadmium cyanide electroplating operations. Results of previous laboratory studies were used as the basis of design for the construction of a pilot-scale system that was installed at the North Island Naval Aviation Depot, San Diego, CA. In this process, a chelating cationic resin in the sodium form is used to remove Cd<sup>2</sup> followed by a strong base anionic resin for removal of free evanide. Tests were conducted using both simulated rinsewaters and actual wastewaters. The results showed that the removal of Cd<sup>+2</sup> was successful in all cases and the effluent concentration was below the Federal Pretreatment Standards in most cases. The success of the cation resin is due to its ability to break the metal cyanide complex and selectively remove Cd<sup>+2</sup> even in the presence of high concentrations of other cations. The removal of CN was not as successful. Effluent concentrations were above Federal discharge standards. The cationic resin was regenerated with sulfuric acid, producing a concentrated solution of cadmium sulfate. Cadmium was recovered from the regenerant solution by electrowinning. The anionic resin was regenerated with sodium hydroxide, producing a concentrated sodium cyanide solution.

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# **Table of Contents**

		•	Page
Execu	itive	Summary E	<b>S-1</b>
1.0	Intro	oduction	1-1
2.0	Bac	kground	2-1
	2.1	Navy Electroplating Operations	2-1
	2.2	Description of Ion Exchange Phenomena	2-1
	2.3	Previous Laboratory Studies	2-2
	2.4	Electrolytic Recovery Phenomena	2-3
3.0	Teci	hnical Objective	3-1
4.0	Pilo	t System Design and Operation	4-1
	4.1	System Description	4-1
	4.2	Basis of Design	4-3
	4.3	System Installation	4-3
	4.4	Description of System Operations	4-5
	4.5	Operating Procedures 4.5.1 Preparation of Wastewater 4.5.2 Preparation of Regeneration Solutions 4.5.3 Loading Columns 4.5.4 System Operation 4.5.5 Regeneration 4.5.5.1 Cation Column Regeneration 4.5.5.2 Anion Column Regeneration	4-13 4-14 4-14 4-15 4-18
	4.6	Sampling Procedures	4-21
5.0	5.1	Summary of Results Column Breakthrough and Resin Capacity 5.2.1 Cation Column Results 5.2.1.1 Cadmium Resin Capacity 5.2.1.2 Compliance with Regulatory Limits 5.2.1.3 Operational Difficulties	5-1 5-4 5-9 5-9 5-17

# Table of Contents (continued)

		Page
	5.2.2 Anion Column Results 5.2.2.1 Cyanide Resin Capacity 5.2.2.2 Compliance with Regulatory Limits 5.2.2.3 Monitoring Cyanide Breakthrough	5-25 5-30
	5.3 Ion Exchange Column Regeneration 5.3.1 Cation Regeneration Results 5.3.1.1 Cadmium Sulfate Elution Curve 5.3.1.2 Cadmium Recovery 5.3.1.3 Acid and Water Requirements 5.3.2 Anion Regeneration Results 5.3.2.1 Sodium Cyanide Elution Curve 5.3.2.2 Cyanide Recovery	5-32 5-32 5-32 5-32 5-36 5-36 5-36
	5.4 Electrolytic Recovery of Cadmium	5-40
6.0	Full-Scale System Design	6-1
	6.1 Cd-CN Rinsewater Treatment System Description	6-1
	6.2 Design Considerations  6.2.1 Feed System - System 100  6.2.2 Cation Exchange System - System 200  6.2.3 Cation Regeneration and Electrolytic Recovery -  System 300  6.2.4 Reverse Osmosis System (RO) - System 400  6.2.5 Cyanide Destruction	6-7 6-10 6-12
7.0	Cost Estimation and Economic Evaluation	7-1
	7.1 Cost Estimation Approach	7-1
	7.2 Capital Investment	7-1
	7.3 Operating Costs	7-3
B.0	Conclusions and Recommendations	8-1
D.O	References	9-1

# Table of Contents (continued)

		Page
Appendices		. 85
Appendix A:	Summary of Sampling and Analytical Procedures	
Appendix B:	Cation Column Breakthrough and Regeneration Curves	
Appendix C:	Anion Column Breakthrough and Regeneration Curves	
Appendix D:	Summary of Analytical Results	
Appendix E:	Equipment List and Costs for Option No. 1	
Appendix F:	Equipment List and Costs for Option No. 2	
Appendix G:	Cost Estimation Approach	
Appendix H:	Calculations	

#### List of Tables

		Page
ES-1	Rinsewater Characterization Data	ES-3
4-1	Basis of Design	4-4
4-2	Proposed Ion Exchange Test Run Matrix	4-16
4-3	Proposed Ion Exchange Test Run Matrix	4-17
4-4	Ion Exchange Regeneration Parameters	4-19
5-1	Summary of Pilot Test Runs for Cation Columns	5-5
5-2	Summary of Pilot Test Runs for Anion Columns	5-6
5-3	Rinsewater Characterization Data	5-8
5-4	Summary of Cation Column Capacity	5-10
5-5	Summary Anion Column Capacity	5-26
5-6	Summary of Regenerations for	5-33
5-7	Summary of Regeneration Recoveries for Cation Columns	5-35
5-8	Typical Cation Column Regeneration (C-3, Regeneration Run RC-3, City Water)	5-38
5-9	Summary of Regenerations for Anion Columns	5-39
5-10	Summary of Regeneration Recoveries for Anion Columns	5-42
5-11	Typical Anion Column Regeneration (A-1, Regeneration Run RA-9, City Water)	5-44
6-1	Rinsewater Characterization for NADEP North Island	6-2
6-2	Summary of Rinse Water Volumes and Chemical	6-11
7-1	Capital Investment Summary for Cd-CN Rinsewater	7-2

# List of Tables (continued)

		Page
7-2	Operating Costs for the Cadmium Cyanide Treatment	. 7-4
7-3	Operating Costs for the Cadmium Cyanide Treatment	. 7-5
7-4	Summary of Power Consumption - Option No. 1	. 7-6
7-5	Summary of Power Consumption - Option No. 2	. 7-7

# List of Figures

		Page
ES-1	Typical Cation Breakthrough Curve	ES-2
ES-2	Typical Anion Breakthrough Curve	ES-2
ES-3	Block Flow Diagram for Full-Scale Cadmium Cyanide Treatment System - Option No. 1	ES-6
ES-4	Block Flow Diagram for Full-Scale Cadmium Cyanide Treatment System - Option No. 2	ES-7
2-1	Predicted Cd2+ Resin Capacities Plotted on Cd-Cation Equilibrium Curves	2-4
2-2	Illustration of Limiting Current for a Fixed	2-6
4-1	Block Flow Diagram for the Pilot-Scale	4-2
4-2	Pilot System Equipment Layout Plan	4-6
4-3	Piping Diagram for Ion Exchange Pilot System	4-8
5-1	Observed Cd2+ Resin Capacities for Each Run Plotted on Cd-Cation Equilibrium Curves	5-12
5-2	Average Cd <sup>2</sup> Resin Capacities for Each Type of Rinsewater Plotted on Cd-Cation Equilibrium Curves	5-13
5-3	Columns C-1 and C-2 Breakthroughs (Runs BC-6 and BC-7) 6/8-6/11	5-15
5-4	Columns C-1 and C-2 Breakthroughs (Runs BC-12 and BC-13) 7/20-7/22	5-16
5-5	Columns C-1 and C-2 Breakthroughs (Runs BC-8, BC-9 and BC-10) 6/15-6/23	5-18
5-6	Dragout Simulation ERU Run	5-19
5-7	Column C-1 Breakthrough (Run BC-11) 6/24-6/25	5-20
5-8	Column A-3 Breakthrough (Run BA-3) 4/14-4/15	5-28
5-9	Column A-1 Breakthrough (Run BA-4) 6/15-6/16	5-29
5-10	Column A-2 Breakthrough (Run BA-7) 6/25	5-31

# List of Figures (continued)

		Page
5-11	Column C-3 Regeneration (Run RC-7) 5/1592	5-34
5-12	Column C-1 Regeneration (Run RC-16) 7/22/92	5-37
5-13	Column A-2 Regeneration (Run RA-4) 4/15/92	5-41
5-14	Column A-1 Regeneration (Run RA-6) 6/18	5-43
5-15	ERU Recovery of Cadmium from Concentrated Cation Eluxe Solution	5-46
6-1	Block Flow Diagram for the Full-Scale Cadmium	6-4
6-2	Block Flow Diagram for the Full-Scale Cadmium	6-5
6-3	Flow Diagram of System 100 - Feed System	6-8
6-4	Flow Diagram of System 200 - Cation Exchange	6-9
6-5	Flow Diagram of System 300 - Cation Regeneration and Electrolytic Recovery	6-13
6-6	Flow Diagram of System 400 - Reverse Osmosis (RO) (Option No. 1 Only)	6-15

# List of Photographs

	Page
4-1	NADEP North Island Plating Shop Looking Out from 4-7 Ion Exchange Treatment System
4-2	Ion Exchange Treatment System
4-3	ERU for Cd Metal Removal from Cation Regenerant
4-4	On-Site Analytical Setup for Cd <sup>2</sup> + and CN- Analysis

#### PREFACE

This report was prepared by Arthur D. Little, Inc., Cambridge, Massachusetts under Contract No. N47408-89-D-1025 for the Naval Civil Engineering Laboratory (NCEL), Port Hueneme, CA.

This document summarizes the work performed between September 1991 and October 1992 on the pilot plant testing and evaluation of an ion exchange process for treatment and recovery of cadmium cyanide wastewater. The pilot plant system was installed and operated at the North Island Naval Aviation Depot, San Diego, CA by Arthur D. Little, Inc. The results obtained during the field testing are documented in this Developmental Test Report. Ms. Jennie L. Koff was the NCEL Project Officer for this contract; Armand A. Balasco and Richard C. Bowen were the project manager and project engineer, respectively, for Arthur D. Little, Inc.

#### **Executive Summary**

Electroplating is performed by the Navy at approximately 36 Naval Activities. Typically, between 1,000 and 50,000 gallons per day (gpd) of cyanide wastewaters are generated at approximately 20 of the 36 Navy plating shops. The Naval Civil Engineering Laboratory (NCEL) has been tasked with the development of alternative technologies for the minimization and cost-effective treatment of cvanide (CN-) laden wastewater generated in these shops. Several technologies are being considered under this program including ion exchange, electrolytic recovery, and reverse osmosis. NCEL has chosen to develop and test an ion exchange metal recovery system to treat dilute cadmiumcyanide (Cd-CN) wastewaters which minimizes the generation of hazardous waste. The system has undergone laboratory-scale studies, pilot system construction, and pilot-scale testing. This report summarizes the results of the pilot scale testing for this specific technology.

Ion exchange removes the soluble ions in water by exchanging a non-toxic ion for those dissolved in the water. The advantages of ion exchange include nearly 100% removal of heavy metals from the wastewater, the potential for recovery of the soluble materials, the ability to reuse the treated water, and the elimination of metal hydroxide sludges. Ion exchange for the treatment of Cd-CN wastewaters was pursued because of indications that the Cd2+, as well as the CN-, could be removed from the wastewater, and be recovered and reused in the plating solution. This would result in a net reduction in water use as well as lower hazardous waste generation.

The first step in the program involved laboratory studies to determine which cation and anion resins would provide the best performance for removal of Cd<sup>2+</sup> and CN<sup>-</sup>. In addition, the laboratory studies evaluated two types of resin regeneration; classical chemical regeneration and acid regeneration followed by a gas permeable membrane for the collection of hydrogen cyanide (HCN) gas. Based on these laboratory tests, the use of selective cation

and anion exchange with classical chemical regeneration was chosen for further study and evaluation.

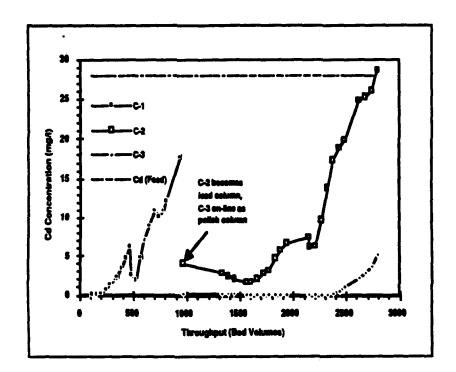
The results of the laboratory studies were used as the basis of design for the construction of a pilot-scale system which was installed at the North Island Naval Aviation Depot, San Diego, CA. North Island was chosen as the host site because it utilizes Cd-CN plating to repair aircraft parts. North Island NADEP generates approximately 1,000 gallons of Cd-CN rinsewater each day.

The test plan developed for the pilot program called for processing rinsewater through the ion exchange columns. To generate rinsewater, concentrated plating solution was diluted to a resulting Cd<sup>2+</sup> concentration of approximately 25 mg/l and a CN-concentration of 50 mg/l. Both city water and water processed through a reverse osmosis (RO) unit were used for dilution. The pilot system was operated with two cation columns in series for the removal of the Cd<sup>2+</sup>, followed by two anion columns in series for removal of CN-. Each resin column contained approximately 2.5 liters of resin and treated approximately 500 ml/min of wastewater. The system was run over a four month period for a total of 7 weeks.

The columns were left on-line until field measurements indicated that the concentration of Cd<sup>2+</sup> and CN- in the effluent were equivalent to the influent concentration or had become constant. Samples were drawn from the effluent on a regular basis and analyzed in order to generate breakthrough curves. Figures ES-1 and ES-2 are examples of a typical cation and anion breakthrough curve obtained during the test program.

The results of the pilot testing indicated that the quality of the dilution water and the concentration of Cd<sup>2+</sup> and CN- had a major effect on the performance of the ion exchange resin. Table ES-1 summarizes the characteristics of the city water, the RO water, and the contents of Tank T-1 (simulated rinsewater made up with both city water and RO water). The

Figure ES-1: Typical Cation Breakthrough Curve



#### Run Summery

Feed Characterization
Process Water - RO Water
CN (mg/L) - 48
Cd (mg/L) - 28
CN:Cd Ratio - 7.4
pH (s.u.) - 10.5
Na (mg/L) - 125
Ca (mg/L) - <1

#### Column Specification

Mg (mg/L) - <1

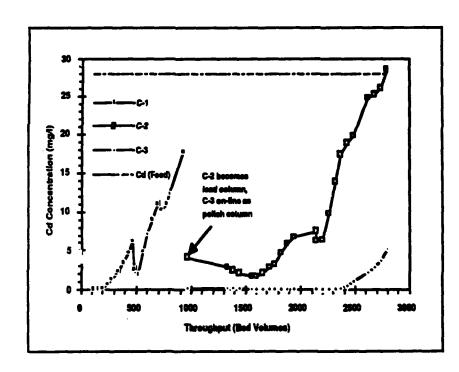
Cation BV (L) - 2.2 Flow Rate (ml/min) C-1: 53 Flow Rate (ml/min) C-2: 70 Flow Rate (ml/min) C-3: 70

#### Results

Cation Capacity (meq/L) C-1: 340
Cation Capacity (meq/L) C-2: 630
Cation Breaktivough (BV) C-1: 1140
Cation Breaktivough (BV) C-2: 1600\*

\* Equivalent BVs of feed

Figure ES-2: Typical Anion Breakthrough Curve



#### **Run Summary**

Feed Characterization
Process Water - RO Water
CN (mg/L) - 47
CN:Cd Molar Ratio - 7.3
pH (s.u.) - 10.5
CO3 (mg/L) - 108
SO4 (mg/L) - 5.1
Cl (mg/L) - 71.4

#### Column Specification

Anion BV (L) - 2.5 Flow Rate (ml/min) - 600

#### Results

CN Capacity (meq/L) - 121 Anion Breakthrough (BV) - 170

Table ES-1: Rinse Water Characterization Data

					Concer	ntration (	mg/L)					1	
Semple Location	pH (s.u.)	CN	Cd Total	Na	Ca.	Mg	Fe	Cu	cos	804	CI	Total Anion (meg/L)	Total Cation (meg/L)
City Water	_		ND	110	86	25	ND	0.2	12	250	110	6.4 ·	111
RO Water	l —	_	-	22	ND	ND	ND	0.0	0.0	3.0	33	1.0	1.0
Plating Rinse Water Tank	_	47	17	190	34	29	0.3	2.1	38	250	160	13	13
T-1 (CW low Cd)	9.6	55	18	220	42	24	0.3	2.9	60	240	170	14	14
T-1 (RO Water)	10.5	50	24	128	ND	ND	0.4	2.0	108	6.0	71	7.6	6.1
T-1 (RO [DO])	11	148	51	416	ND	ND	1.0	10	382	7.8	301	27	19
T-1 (CW high Cd)	9.8	71	66	301	14	23	1.0	3.0	78	196	177	14	17

-- Not analyzed for

ND - Not Detected

CW - city water

Source: Arthur D. Little, Inc.

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city water in the San Diego area contains high concentrations of Ca<sup>2+</sup>, Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and Cl.- These dissolved solids added to the ionic loading to the resin and reduced its capacity to remove Cd<sup>2+</sup> and CN. Four different types of cadmium plating rinsewater were processed including: city water with low concentration of Cd<sup>2+</sup> and CN-: city water with high concentrations of Cd<sup>2+</sup> and CN- (actual rinsewater); RO water with low concentrations of Cd<sup>2+</sup> and CN-; and RO water treated by an electrolytic recovery unit (as might be seen in a dragout rinse).

The removal of Cd2+ was successful in all cases and the effluent Cd2+ concentration was below the Federal Pretreatment Standard of 0.69 mg/L (daily maximum) in most cases. Some Cd2+ leakage did occur from freshly regenerated columns, however, it is believed that it can be controlled by performing slower regeneration sequences and lowering the throughput flow rate. The success of the cation resin is due to its ability to selectively remove the Cd2+ even in the presence of high concentrations of other cations as in the city water. The Cd<sup>2+</sup> resin capacities followed the same relationship as observed in the earlier laboratory study: Cd2+ resin capacity increases as the non-Cd2+ cation concentration of the solution decreases: and Cd<sup>2+</sup> resin capacity increases as the non-Cd<sup>2+</sup> cation:Cd molar ratio decreases.

The removal of CN-, however, was not as successful. The anion resin is not as selective, therefore, much of the CN-passed through the system into the effluent. The effluent concentrations were above the Federal Pretreatment Standard of 1.2 mg/L within a few bed volumes of the start of processing. This was observed when using both city water and RO water. In addition, the results showed that as the CN- concentration decreased, the resin CN- capacity decreased as was demonstrated in the previous laboratory study.

Sulfuric acid was used to regenerate the cation columns. The acid regeneration

sequence produced a concentrated solution of cadmium sulfate (CdSO<sub>4</sub>) which was then able to be processed in the electrolytic recovery unit (ERU). The flow rate of acid, over the range tested. appeared to have a slight effect on the efficiency of the regeneration procedure in that the slower flow rates resulted in a narrower elution curve. The majority of the Cd<sup>2+</sup> was recovered in 1.5 to 3 bed volumes (BV) of total throughput and resulted in a CdSO<sub>4</sub> solution with approximately 2000 mg/l of Cd<sup>2+</sup>. Typical Cd<sup>2+</sup> recoveries ranged from 75 to 100%. Periodic samples were taken during regeneration to develop a bell curve allowing the collection of the most concentrated solution for processing in the ERU. Following acid regeneration. the resin was put into its sodium form by processing sodium hydroxide (NaOH) through the column.

The anion columns were regenerated with NaOH. Cyanide recoveries ranged from 12 to 15% and the concentration of the NaCN regenerant was low (<500 mg/l CN-). This is due to the poor removal of CN- by the resin, the gradual decomposition of the CN- to cyanate (CNO-), and the removal of CN- from the resin during the initial rinse. In addition, analysis of the regenerant solution showed high concentrations of the other anion species present in the rinsewater which were also removed on the anion resin. These species included SO<sub>4</sub><sup>2</sup>·, Cl-, and CNO. The high concentrations of these anions and the low concentration of CN- make the reuse of the NaCN solution in the plating bath undesirable.

Electrolytic recovery tests were performed to determine the feasibility of recovering Cd metal from concentrated solutions. Two electrolytic recovery tests were conducted; one on the concentrated CdSO<sub>4</sub> regenerant solution, and one on a simulated dragout (DO) solution. The first test was conducted on the concentrated regenerant (2000 mg/l Cd<sup>2+</sup>) during which 97% of the cadmium was recovered. The solution was extremely acidic and resulted in a powdery deposit of Cd metal on the cathode plates. Low recirculation and a high current density

added to the poor quality of the plate. This can be improved by increasing the pH, lowering the current density, and increasing the recirculation rate.

The second ERU test was conducted on a simulated dragout solution prepared by diluting concentrated plating solution to a CN- concentration of 1,800 mg/l and a Cd2+ concentration of 1,000 mg/l. Approximately 65% of the cadmium was recovered before the test was terminated. The recovered Cd metal was of much higher quality than the previous test, being thin silvery sheets. This is due to the higher recirculation rate, lower current density, and higher pH of the cyanide based-solution. The ERU tests indicate that Cd metal can be recovered from both concentrated regenerant solutions and dragout solutions.

Based on these results, a preliminary design was prepared of a full-scale system. Two systems were evaluated; one utilizing RO water for rinsewater makeup (Option No. 1), and one utilizing city water (Option No. 2). Both systems utilize ion exchange for the removal of Cd<sup>2+</sup>, however, the use of ion exchange for the removal of CN- was not included due to the poor results seen in the pilot study. CN- treatment was assumed to be alkaline chlorination which is part of the existing North Island industrial wastewater treatment plant (IWTP).

Figure ES-3 illustrates the block flow diagram for Option No. 1.

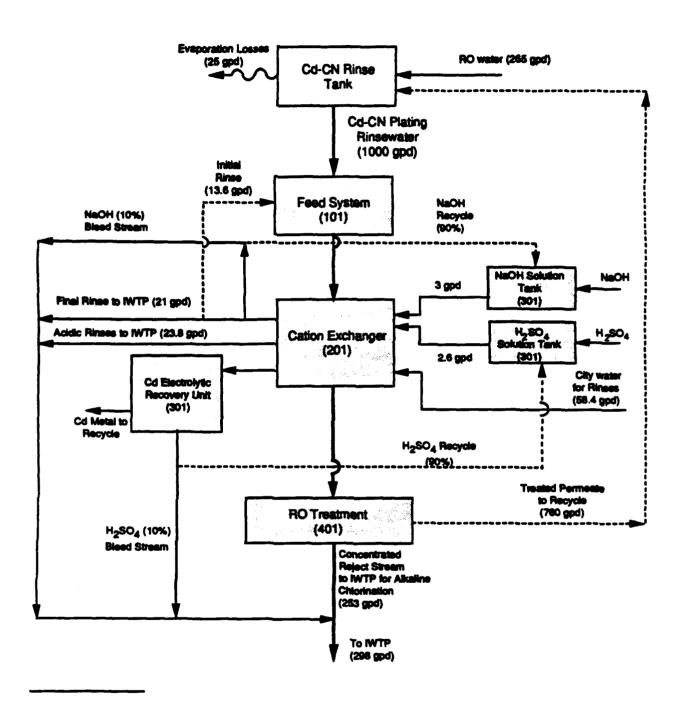
Approximately 75% of the treated water is recycled back to the Cd-CN rinse tank (or other rinse tank). In addition, because RO water is used as make up to the rinse tank, the cation loading to the ion exchange columns is reduced and the volume of resin required is less.

Figure ES-4 illustrates the block flow diagram for Option No. 2. Only city water is utilized in this system and no treated water is recycled. This results in the need for larger volumes of resin to treat equal volumes of water. This also results in larger quantities of regenerant chemicals and larger holding tanks.

A comparison of the capital and operating costs of the two Options was conducted. The capital costs are essentially the same, \$210,000 for Option No. 1 and 204,000 for Option No. 2. The operating costs, however, were lower for Option No. 1 than for Option No. 2 due to the recycling of approximately 75% of the rinsewater. and the lower chemical and power requirements. Annual operating costs were estimated to be \$68,000 for Option No. 1 and \$71,000 for Option No. 2. It appears from this analysis that RO treated water, or water of similar quality, is desirable for use in plating rinse tanks when utilizing ion exchange as a treatment technology.

These capital and operating costs were compared to costs developed in an earlier study for a conventional treatment system including metals precipitation and cyanide destruction. The capital cost was estimated at \$115,000 and the annual operating costs at \$47,000. These costs are lower than those developed for the ion exchange system, however, the hidden costs of hazardous waste generation should be considered when making a comparison.

Figure ES-3: Block Flow Diagram for Full-Scale Cadmium Cyanide Treatment System - Option No. 1

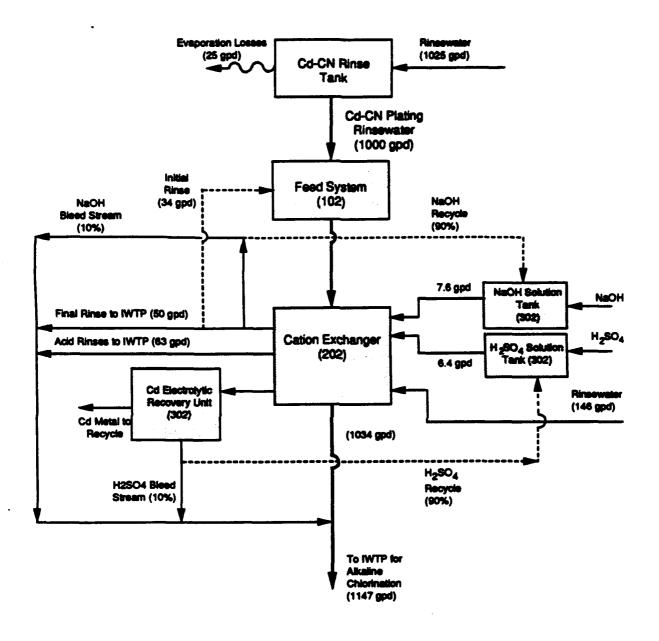


NOTE: Regeneration rinse volumes are averaged to a gas or per day volume, based on regeneration sequences being parformed once every five days.

Source: Arthur D. Little, Inc.

- System included in full-scale design and capital cost estimate.

Figure ES-4: Block Flow Diagram for Full-Scale Cadmium Cyanide Treatment System - Option No. 2



NOTE: Regeneration rinse volumes are averaged to a gallon per day volume, based on regeneration sequences being performed once every five days.

- System included in full-scale design and capital cost estimate.

Source: Arthur D. Little, Inc.

#### 1.0 Introduction

The Naval Civil Engineering Laboratory (NCEL) has been tasked with the development of alternative technologies for the minimization and cost-effective treatment of cyanide (CN-) laden wastewater generated in Naval plating shops. Under this program, NCEL is developing an ion exchange metal recovery system to treat dilute metal-CN- wastewaters without generating hazardous sludge.

Laboratory studies were completed on the following ion exchange/metal recovery systems: (1) Heavy-metal selective cation exchange in conjunction with strong base anion exchange; and (2) Anion exchange/gas membrane (program performed in conjunction with the University of Minnesota). The results of the laboratory tests indicated that selective cation exchange and anion exchange systems should be further developed and evaluated. Recent advancements in ion exchange technology indicate that specific contaminants can be removed selectively. The unique process can be applied to the treatment of cyanide wastewater and involves the use of chelating cation resin followed by a strong base anion resin. Heavy metals such as cadmium that are complexed with cyanide in an anion species are not normally displaced by sodium in a cation resin. However, the laboratory tests indicated that a chelating cation resin in the sodium form would break the metal cyanide complex and adsorb cadmium. Free cyanide passing through the resin is then removed by a strong base anion resin. Regeneration of the spent cation resin is performed using sulfuric acid, producing a concentrated metal acid solution that is treated using electrowinning to recover the cadmium metal for reuse. Regeneration of the spent anion resin is performed using sodium hydroxide, producing a concentrated sodium cyanide solution.

Developmental testing and evaluation of this technology has been conducted in several phases: design and construction of a pilot system; hazards and operability (HAZOP) analysis of the pilot system; installation and operation of the pilot system at North Island Naval Aviation Depot (NADEP); evaluation of the operating data collected during the pilot testing; economic evaluation of the ion exchange system; and the preparation of a Developmental Test Report (DTR). This report details the results of the developmental test and evaluation effort completed at NADEP North Island on the ion exchange/metal recovery process.

#### 2.0 Background

#### 2.1 Navy Electroplating Operations

Electroplating is performed by the Navy at approximately 36 Naval Activities. The electroplating process is used to repair parts from aircraft, ships, weapons, and communications systems. Approximately 20 of the 36 plating facilities use cyanide solutions to plate metals such as cadmium, copper, zinc, silver, nickel, and gold. Typically, between 1,000 and 50,000 gallons per day of cyanide-containing rinsewaters are generated at the 20 plating facilities utilizing cyanide plating operations. The most common method of treatment of these waste waters is alkaline chlorination of the cyanide followed by hydroxide precipitation of the heavy metals. These two treatment methods are classic "end of pipe" technologies, and therefore, do not provide the ability to recover, recycle or reuse the contaminants (metals and cyanide) or the treated rinsewater. In addition, the hydroxide precipitation of heavy metals generates a metal hydroxide sludge which must be disposed of as a hazardous waste.

In the past, these treatment technologies have been satisfactory in meeting regulatory requirements for wastewater discharges, however, it is likely that these requirements will become more stringent especially for cadmium and cyanide. In addition, the Resource Conservation and Recovery Act (RCRA) instituting the cradle to grave management of hazardous waste discourages the generation of any hazardous waste and mandates the active pursuit of source reduction and waste minimization efforts in manufacturing processes. The study of ion exchange and electrolytic recovery for the treatment and reuse of cadmium and cyanide is an effort to reduce the liability of generating hazardous waste and to comply with the RCRA waste minimization requirements.

#### 2.2 Description of ion Exchange Phenomena

Ion exchange is the physical-chemical process by which ions in solution are transferred to a solid, and vice versa. The ions are held by electrostatic forces to charged functional groups on the surface of a solid, and are exchanged for ions in solution. The solids are usually in the form of resins, and consist of small beads with functional groups on the surface available for ion exchange. The charge of the functional group determines the type of ion which is attracted to it, cation or anion. Cation exchange resins typically contain sulfonic acid groups which are negatively charged and attract positively charged cations. Anion resins contain amine-based functional groups which are positively charged and are electrostatically attractive to negatively charged anions. All ion exchange resins have fixed ionic groups that are balanced by counter-ions of opposite charge to maintain a neutral charge. These counter-ions will exchange with the ions in solution.

In the typical mode of operation, the ion exchange resin is contacted with the solution containing the ion to be removed until the active sites in the resin partially or completely

contain that ion ("exhausted"). Following the exhaustion step, the resin is contacted with a concentrated solution of the ion originally associated with the resin to convert ("regenerate") the resin back to its original ionic form. Typical cation regeneration solutions are sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solutions, or sodium chloride (NaCl) solutions, to replace the ion attached to the functional group with either H+ or Na+. The resulting "eluate solution" contains high concentrations of the ion removed from solution. A similar process is used for anion regeneration. Typical regeneration solutions for anion resins are sodium hydroxide (NaOH) or NaCl, which put the resin into the OH- or Cl-form.

#### 2.3 Previous Laboratory Studies

NCEL completed a screening of chelating resins and an initial feasibility study 5 on the selected resin. The results of their screening indicated that Rohm and Haas' Amberlite IRC-718<sup>TM</sup>, a macroreticular chelating resin, was not only the most effective resin tested in breaking the heavy metal Cd-CN complex, but also had the highest selectivity for the Cd<sup>2+</sup> ion. At the conclusion of the screening tests, NCEL recommended the process be reviewed further for technical feasibility in a laboratory program.

Both of the ion exchange systems proved technically feasible and capable of recovering the Cd<sup>2+</sup> and CN-. One of the initial concerns regarding the cation/anion exchange system was the ability of the cation exchange resin, Amberlite IRC-718<sup>TM</sup>, to break the Cd-CN complex and retain only free Cd<sup>2+</sup> on the resin. The results<sup>6</sup> of both isotherm and column tests demonstrated that the cation resin was capable of breaking the complex and binding the free Cd<sup>2+</sup>. The laboratory tests<sup>6</sup> also showed that the Cd<sup>2+</sup> capacity of the resin was dependent on the sodium (Na<sup>+</sup>) concentration in the feed stream, and that the Cd<sup>2+</sup> capacity increased when: 1) the total cation concentration of the solution decreased, even at a constant relative concentration of Na<sup>+</sup> and Cd<sup>2+</sup> (molar ratio); and 2) the Na<sup>+</sup>:Cd<sup>2+</sup> molar ratio was small.

The results of the laboratory tests<sup>6</sup> were utilized to develop a model to predict the Cd<sup>2+</sup> resin capacity based upon the total cation concentration in the solution. The model is based upon the following chemical equation:

The equilibrium constant for this exchange can be expressed as follows:

$$K = ([Cd^{2+}]_R * [Na+]_S^2) / ([Cd^{2+}]_S * [Na+]_R^2)$$
 (eq. 2-2)

A median value of K was developed from the laboratory results and was used to solve for the Cd<sup>2+</sup> resin capacity in Equation 2-2 ([Cd<sup>2+</sup>]<sub>R</sub>). Figure 2-1 is a graph produced using this equation where the cation concentration is converted to equivalent Na+ concentration. The graph indicates that the resin has a higher capacity for Cd<sup>2+</sup> when: (1) the ionic concentration of the solution decreases, even though the relative concentration of the Na+ and Cd<sup>2+</sup> (molar ratio) remains the same; and (2) the Na+:Cd<sup>2+</sup> molar ratio decreases. A similar model was developed for the CN- resin capacity in the anion column which showed that the CN- resin capacity increased when the OH- (or total anion concentration) was low and when the CN- was high.

The limitation of the cation/anion exchange system was the capacity of the anion resin, Amberlite IRA-458<sup>TM</sup>, for free CN- at the pH and total anion concentration found in the plating rinsewaters. The resin was technically capable of removing the CN-, however, the resin CN- capacity was very low which results in frequent regeneration. A second limitation of the system was the low concentration of CN- in the NaOH eluate leaving the anion bed and the resulting large volume of eluate to be recycled to the plating bath.

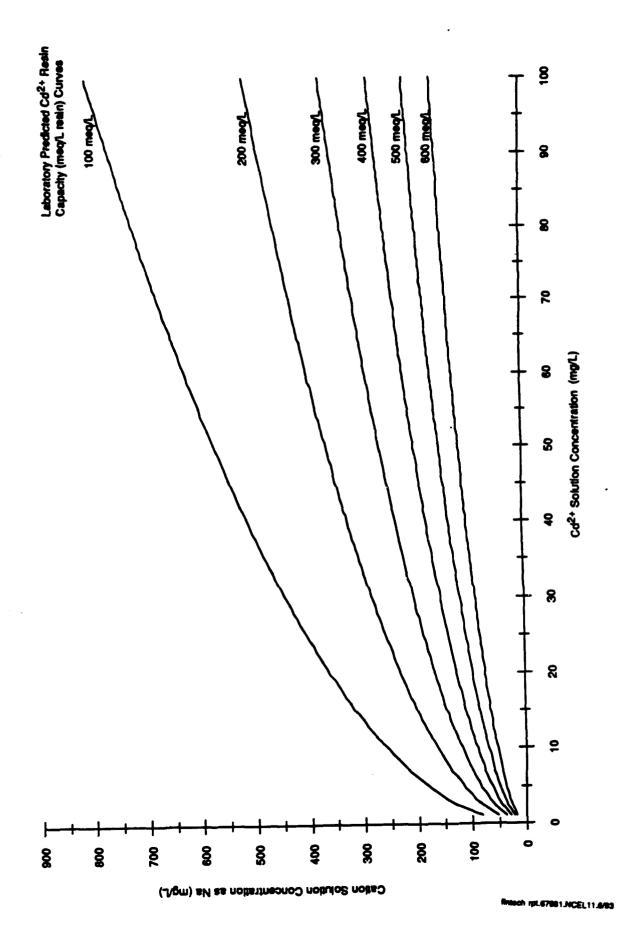
A second process was also investigated which was based on past work by the University of Minnesota 1,2,3,4. This work suggested that a regeneration process using sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) as the regenerant and a gas permeable membrane to collect the hydrogen cyanide (HCN) gas produced would alleviate the metal hydroxide formation during regeneration and allow for the collection of concentrated metal sulfate and sodium cyanide (NaCN) streams. The ion exchange/gas membrane (IX/GM) process was tested and the results were promising, however, it was not selected for further study because of the inability of the process to bind free CN- on the anion resin and because of safety concerns about the intentional production of HCN gas.

#### 2.4 Electrolytic Recovery Phenomena

Electrolytic recovery involves the application of an electric current to an anode, which provides excess electrons to the electrolyte solution. This electric potential drives the metal ions to the cathode plate where the excess electrons are accepted by the metal ion and plated onto the cathode as elemental metal. The principle benefit is that the process is selective, recovering only the metal segment in the waste. In addition, the physical form in which the metal is recovered, its base metallic state, can be potentially reused instead of requiring disposal as a hazardous waste.

Several resistances may be encountered that reduce the efficiency and quality of the plating process and are related to the thickness of the boundary layer (which is a function of circulation rate), the bulk concentration, and the voltage. The typical physical factors used to adjust the rate of metal deposition include cell voltage,

Figure 2-1: Predicted Cd<sup>2+</sup> Resin Capacities Plotted on Cd-Cation Equilibrium Curves



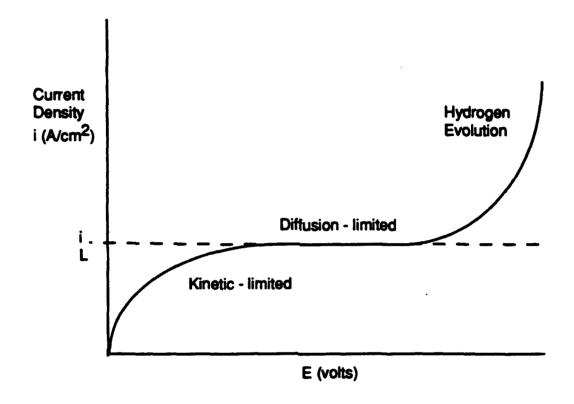
Source: Arthur D. Little, Inc.

current density, cathode surface area, agitation or circulation rate, metal concentration and solution chemistry, and temperature. These factors affect the diffusion rate of metal ions from the bulk solution to the cathode surface where metal ions are reduced to their metallic state and are generally varied to obtain the best conditions for operation. To obtain a good quality deposit, it is desired to keep this process kinetically controlled, as opposed to diffusion controlled. At lower current densities, the metal deposits in an orderly fashion, and the plate is of higher quality. This generally occurs below what is termed the limiting current, or i<sub>L</sub>. Below this current, the process is kinetically limited, above this current, the process is diffusion limited. An illustration of the limiting current is provided in Figure 2-2.

It is especially difficult to operate below i<sub>L</sub> in the lower concentration ranges encountered during waste treatment as opposed to the higher concentrations found in electroplating process tanks. As the concentration decreases, the limiting current also decreases. In addition, in acidic solutions, such as CdSO<sub>4</sub>, with high concentrations of hydronium ions (H<sub>3</sub>O+), the evolution of hydrogen gas is kinetically favored over cadmium deposition which causes a rough powdery deposit because sites of bubble growth are isolated from the electrolyte.

The Navy has conducted considerable research on the use of electrolytic recovery as a point source treatment technology. Several Navy facilities are currently utilizing the technology, however, it is not yet been used in conjunction with ion exchange for removal of the residual soluble metals.

Figure 2-2: Illustration of Limiting Current for a Fixed Metal Concentration



Source: Arthur D. Little, Inc.

#### 3.0 Technical Objective

The overall objective of this program was to determine the ability of the ion exchange system to treat and recover Cd<sup>2+</sup> and CN- from plating rinsewaters. The specific objective of the pilot test program is to utilize the optimum operating conditions for the cation/anion exchange system, as developed in the laboratory<sup>6</sup> for treating synthetic wastewater, to treat actual wastewater. Operation of the pilot system will provide insight into resin capacity, optimum regeneration conditions, process safety issues, process monitoring, emergency procedures, and performance of field instrumentation.

The pilot system was operated for approximately seven weeks using Cd-CN wastewaters generated from NADEP North Island's plating operations during which approximately 17 cation regeneration cycles and 10 anion regeneration cycles were conducted. The system was operated in such a manner as to collect the following types of data:

- Cation and anion resin capacity for Cd<sup>2+</sup> and CN-respectively;
- Cation and anion resin capacity for Cd<sup>2+</sup> and CN- for rinsewaters generated following point source electrolytic recovery;
- Changes in Cd<sup>2+</sup> or CN<sup>-</sup> resin capacity and removal efficiency after a number of regeneration cycles;
- Discharge leakage levels of Cd<sup>2+</sup> and CN<sup>-</sup> after regeneration;
- Concentration of Cd<sup>2+</sup> and CN<sup>-</sup> in the eluate streams:
- Potential for CN-recovery;
- Efficiency of Cd and sulfuric acid recovery in the electrolytic recovery unit;
- Cation resin regeneration efficiency using recovered sulfuric acid;
- Water/rinsewater requirements:
- Energy requirements;
- Material requirements; and
- Operational issues/concerns.

#### 4.0 Pilot System Design and Operation

The pilot system (designed and constructed by Arthur D. Little personnel) was shipped from Arthur D. Little's Cambridge, Massachusetts, facility to North Island as a skid mounted unit. Arthur D. Little personnel began assembling the system on 1 April 1992. The system was started up and operated for seven weeks during the period of 8 April to 24 July 1992. A total of 13 breakthrough curves were developed for the cation columns and seven breakthrough curves for the anion columns. In addition, 17 regeneration curves were developed for the cation columns and 10 for the anion columns. Two electrolytic recovery runs were conducted for the removal of metallic cadmium from solution.

The main parameters influencing the design and operation of the pilot system include:

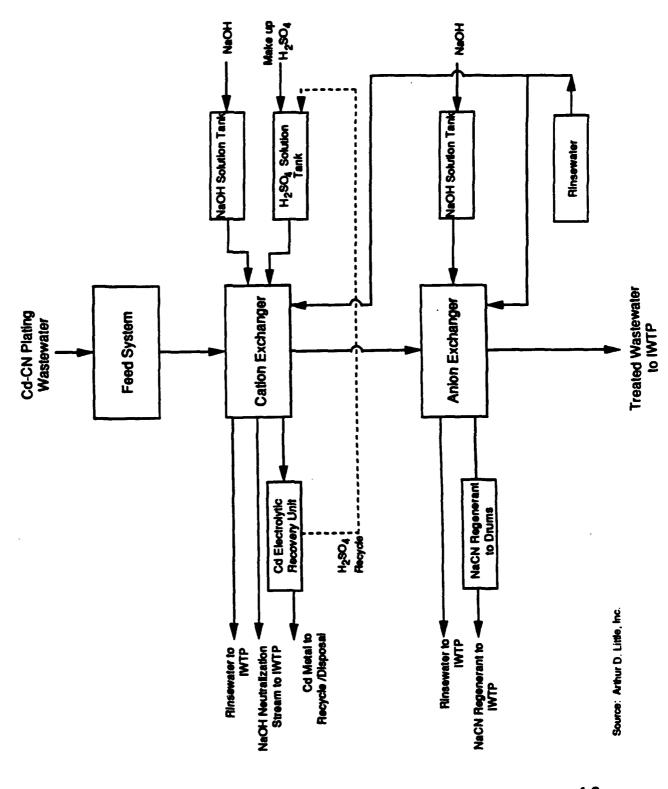
- Hydraulic loading to columns (influent flow rate);
- Pollutant loading (concentration of Cd<sup>2+</sup> and CN-);
- Frequency of regeneration (resin capacity); and
- Rate of regeneration (regenerant flow rate).

During the laboratory testing phase, these operational parameters were varied to determine the optimum conditions for processing Cd-CN wastewaters. These parameters were utilized to size the columns and set the flow rates for the pilot-scale system.

#### 4.1 System Description

Figure 4-1 illustrates the process flow of the pilot system. Cd-CN rinsewater is either transferred directly to the feed system, or plating solution is diluted in the feed system to simulate rinsewater. The rinsewater is then pumped through the cation exchangers to remove the Cd<sup>2+</sup> allowing the free cyanide to pass through and be removed in the anion exchangers. The system design includes three cation columns followed by three anion columns. Two cation columns were utilized in series and two anion columns in series. The third column is left off-line as a spare and is put on-line when the lead column becomes exhausted. The polish column then becomes the lead column, and the spare column is put on-line as the polish column. This design allows two columns to continue operating to maximize resin utilization while the third column is being regenerated. The columns have been designed to minimize the potential for cross contamination of the acid and CN- bearing rinsewaters. Quick disconnect fittings are utilized to add flexibility to the system configuration/operation.

Figure 4-1: Block Flow Diagram for the Pilot-Scale Cadmium Cyanide Recovery System



4-2

Regeneration of the cation columns is conducted in several steps. The column is rinsed to displace any residual cyanide, and is then regenerated utilizing a 10% H<sub>2</sub>SO<sub>4</sub> solution. The most concentrated portion of the CdSO<sub>4</sub> solution is collected in a tank for processing in an ERU to remove the Cd metal. The resin is further rinsed to displace all of the acid. This is followed by an NaOH neutralization step utilizing 5% NaOH and then a final rinse. Anion columns are regenerated in a similar manner utilizing an NaOH solution. The columns are rinsed initially, then the regenerant is metered into the column, and the column is rinsed again to remove any residual NaOH.

During the operation of the pilot system, all treated rinsewater was discharged to the industrial wastewater treatment plant (IWTP) via the cyanide sump in the electroplating shop. All concentrated and dilute acid eluate and rinse solutions were collected in storage tanks and pH adjusted prior to discharge to the IWTP via the same cyanide sump. All concentrated NaCN eluate solutions were removed by the site chemical handlers. The dilute NaCN rinses were discharged to the IWTP.

#### 4.2 Basis of Design

Table 4-1 shows the design basis for the pilot system which reflects the information gathered during the laboratory testing phase and specific conditions found at the NADEP North Island facility, as well as practical items for operating the system efficiently.

Based upon these resin quantities and assumed wastewater concentrations, the lead cation column was estimated to require regeneration every 2 to 3 days, and the lead anion column every 1 to 2 days. These breakthrough periods are dependent upon many factors including: pollutant concentration, flow rate, and regeneration efficiency. The regeneration procedures were developed based on the design basis shown above, the laboratory-scale tests, and from discussions with Rohm and Haas' technical personnel.

#### 4.3 System Installation

The pilot system was fabricated at Arthur D. Little and shipped to NADEP North Island as a skid mounted unit. Arthur D. Little personnel arrived on the NADEP North Island site to begin the installation and start-up of the pilot ion exchange system on 1 April 1992. During this phase, a determination was made that the pilot system was located directly above the general sump which collects acidic wastewaters from the plating shop. In order to prevent any CN- bearing rinsewaters from draining into this sump, it was

# Table 4-1: Basis of Design

#### Parameter

# Quantity

Pilot Plant Operating Schedule Wastewater input flow rate Cd2+ Concentration	24 hrs/day (7 days/week)
	150 gpd
	23 mg/L
CN- Concentration	23 mg/L

### Cation Column Diameter

Length
Flow-through Rate
Hydraulic Loading
Resin Capacity
Bed Volume (BV)

3 in 10 in 20 BV/hr 83 L/min-m<sup>2</sup> 600 meq/L 2.2 L/column

#### Anion Column

Diameter
Length
Flow-through Rate
Hydraulic Loading
Resin Capacity
Bed Volume (BV)

4 in 12 in 10 BV/hr ..3 L/min-m<sup>2</sup> 400 meq/L

2.5 L/column

# Electrolytic Recovery Unit

Capacity
Cathodes
Anodes
Rectifier

20 L 1 s.f. Stainless Steel 1 s.f. Stainless Steel 100 A, 110 V decided that all tanks associated with the ion exchange pilot system be provided with secondary containment, and that all water containing CN- be discharged via a floor drain directly to the CN- sump. Piping alterations were required to accomplish this. In addition to the containment tanks, the ion exchange skids were surrounded with spill containment pillows to prevent any leakage of CN- bearing water from running onto the floor and possibly entering the general sump. Figure 4-2 illustrates the equipment layout of the system in the Building 472 Plating Shop.

After assembly, the pilot ion exchange system was inspected and approved by the NADEP North Island safety and environmental personnel. Upon completion of the installation, the pilot system was started up. Arrangements were made with NADEP second-shift personnel to periodically inspect the system up until 0200 hours each morning; thus allowing the system to continue to operate overnight. The system was operated for a total of seven weeks during the period of 8 April to 24 July 1992. Each ion exchange column was operated until field measurements indicated breakthrough, at which time it was taken off-line and regenerated.

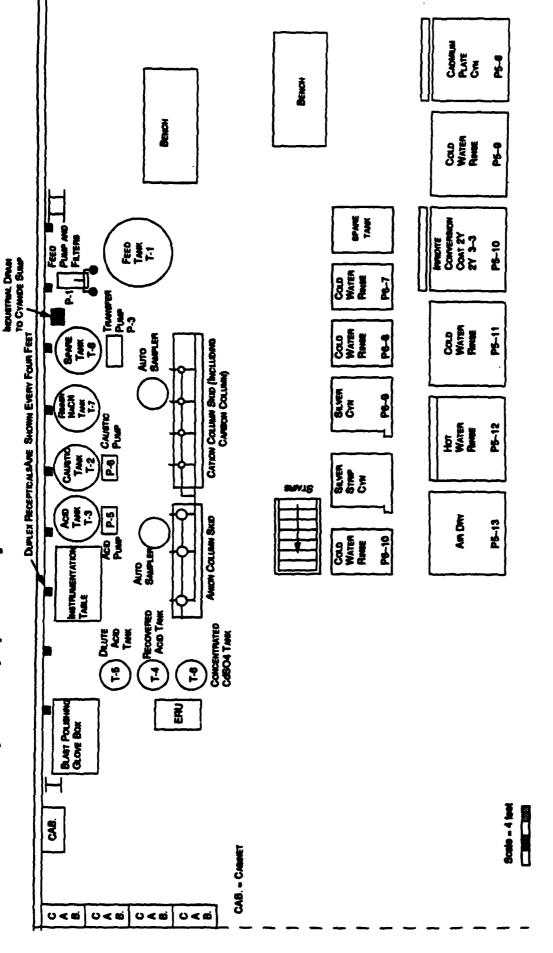
#### 4.4 Description of System Operations

The pilot system is designed to treat rinsewater containing Cd-CN from plating operations in the facility (Photograph 4-1). The wastewater to be treated was obtained from two sources; diluted plating bath solutions and actual plating bath rinsewater. Due to the fluctuations in concentration of the actual rinsewater, most of the tests were conducted on diluted plating bath solutions.

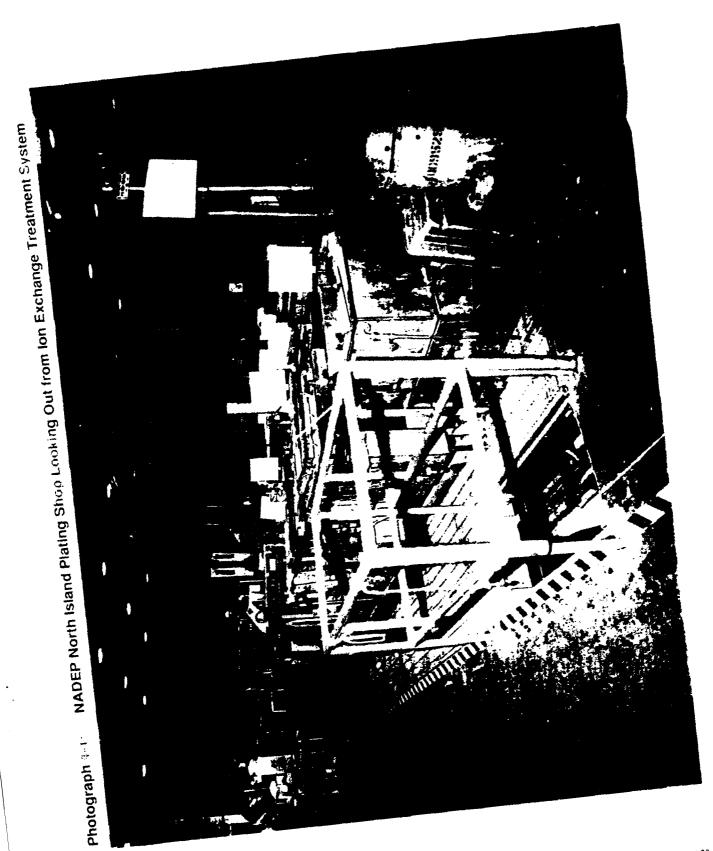
Figure 4-3 is a piping diagram for the pilot system and Photograph 4-2 presents an overview of the system. The wastewater was prepared in the wastewater feed tank (T-1), and pumped through the ion exchange columns. The wastewater was processed through a filter to remove any suspended solids, an activated-carbon column to remove any organic matter (this step was not utilized since organic levels were already sufficiently low), then through the cation columns, followed by anion columns in series. One cation column and one anion column were always off-line to allow for regeneration. The treated effluent was then discharged to NADEP North Island's Industrial Wastewater Treatment Plant (IWTP) via the CN- sump in Building 472. Throughout the conduct of the test, parameters such as flow rate and pressure drop along with concentration data were collected (at specified locations throughout the pilot system) to allow for evaluation of the process.

Upon breakthrough, the lead anion and cation columns were taken off-line and regenerated, and another column was put on-line. The system had been designed to allow the lead column (both cation and anion) to be taken out of service for regeneration, allowing the remaining two columns to continue to process wastewater. Upon completion

Figure 4-2: Pilot System Equipment Layout Plan



SOURCE: NADEP North Island and Arthur D. Lutte, Inc.



To Building 472 Cyanide Sump Equipment legend follows 6:3 Caston Resin Beds **8**-0 AV 15 PM A:3 Anton Resin Bads Regenerant Feed Tanks Ş ₩ 6 A-2 Activated Carbon Bed ¥:1 (2) AS AS 1-8 ¥ ¥ Cd Electrolytic Recovery Unit ¥ ¥ T-7 1-5 Effluent Tanks Source: Arthur D. Little, Inc. Wastewater Food Tank 1-6 **1-4** ¥ ¥ ¥ **( 3** 

Figure 4-3: Pipling Diagram for Ion Exchange Pilot System

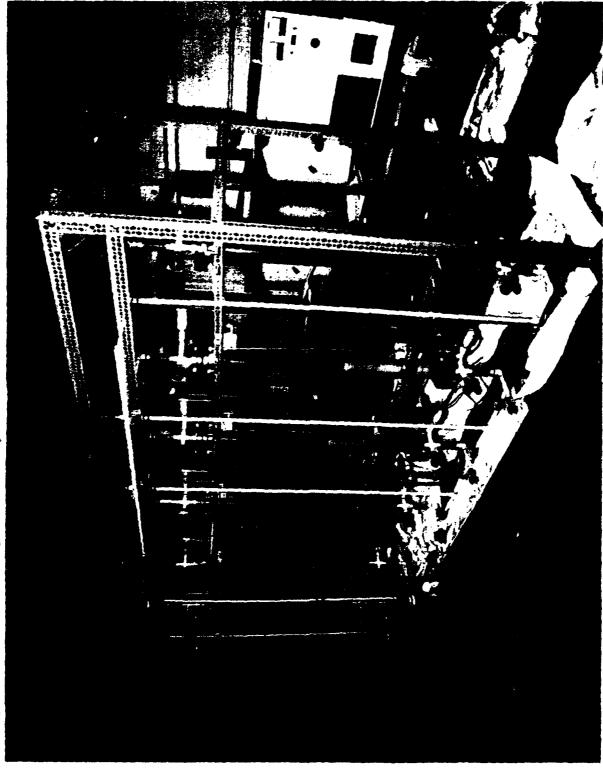
Figure 4-3 (continued): Legend for Piping Diagram

	Hard Piping
	Flexible Hose with Quick Disconnects
Ø	Centrifugal Pump P-1 Feed Pump P-2 Feed Pump P-3 Transfer Pump P-4 Transfer Pump
<b>□-□</b>	Gear or Peristaltic Pump P-5 Sulfuric Acid Pump P-6 Sodium Hydroxide Pump
<b>©</b>	Pressure Indicator
$\mathbf{\Theta}$	Pressure Differential Indicator
igoremsize	Filter
<b>@</b>	pH Meter
	Ion Specific Meter
toCs	Sample Point
<b>6</b>	Temperature Meter
	Rotometer
post	Bail Valve
Ė	Vent Valve
C	Quick Disconnect
	Influent Tank T-1 Wastewater Feed
	Chemical Feed Tanks T-2 Sodium Hydroxide T-3 Sulfuric Acid
Sampling	Effluent Tanks T-4 Regenerated Sulfuric Acid T-5 Dilute Sulfuric Acid T-6 Concentrated Cadmium Sulfate T-7 Regenerant Sodium Cyanide T-8 Spare Tank
Arrangement:	And/Or (#)
(Ce s)	Auto Sampler

Intech 191,67881.NCEL11,983

4-8

Source: Arthur D. Little, Inc.



Photograph 4-2: Ion Exchange Treatment System

of the regeneration sequence, the freshly regenerated column was placed in standby until it was required to be returned to service as the polishing column (last in series). This enabled the resin in the remaining two columns to be utilized to their full capacity. Some runs were conducted without a polish column on-line when a breakthrough curve for just the lead column was being developed.

Regeneration of the cation columns involves a downflow rinse step utilizing city water, followed by the regeneration step where a solution of 10% H<sub>2</sub>SO<sub>4</sub> is passed through the resin column to remove the Cd<sup>2+</sup> ions as CdSO<sub>4</sub>. The concentration of CdSO<sub>4</sub> in the waste eluate solution varies, beginning with very dilute concentrations, followed by a highly concentrated solution, followed by a dilute concentration again. This "bell curve" was characterized during the pilot phase from the data collected. After completion of the regeneration phase, a second rinse is performed to displace the H<sub>2</sub>SO<sub>4</sub> solution from the cation column. Finally, the resin is neutralized with a 5% NaOH solution to put the resin back in the "sodium" form. A final rinse is performed to remove any residual NaOH from the column. The different solutions were collected in the Dilute Sulfuric Acid Tank (T-5), the Concentrated CdSO<sub>4</sub> Tank (T-6) depending upon the concentration of Cd<sup>2+</sup> and the pH, and the Spare Tank (T-8). The redirection of the wastewater to these tanks was controlled manually.

Regeneration of the anion columns involves a similar rinse-regeneration-rinse sequence. The regeneration solution, however, is 5% NaOH solution. The resulting eluate contains varying concentrations of NaCN at a pH varying from 10 to 13. Because of the potential high concentrations of NaCN in the eluate, it was collected in the NaCN Tank (T-7) where it was held until the NADEP North Island chemical handlers emptied the tank.

Two ERUs were utilized to remove Cd metal from solution. Photograph 4-3 shows the ERU used to recover Cd metal from the cation eluate. Each ERU unit was operated in a batch mode. The recirculation pump suction line was piped from the process tank discharging to the unit. The liquid level would rise and overflow through an overflow pipeline back into the process tank. The current was adjusted as necessary. Each night when the unit was shut down the cathodes were removed, rinsed, and scraped. The clean cathodes were reinserted into the unit upon start-up of the next sequence. The current density, agitation rate, and Cd<sup>2+</sup> concentration were monitored to determine the operating conditions.

Photograph 4-3: ERU for Cd Metal Removal from Cation Regenerant

# 4.5 Operating Procedures

# 4.5.1 Preparation of Wastewater

The wastewater to be processed through the pilot ion exchange system was collected and prepared from two sources: 1) dilution of the plating bath solution at a ratio of approximately 1000:1 in T-1; and 2) transfer of the rinsewater directly from the plating bath rinse tank to T-1.

Prior to collecting the wastewater samples, the NADEP North Island Shop Materials Manager was contacted to ensure that the collection procedure would not interrupt normal production. The materials manager collected all samples taken from the plating bath. The shop chemical handlers were contacted to transfer rinsewater from the Cd-CN rinsewater tank to Tank T-1.

Based upon an analysis of the plating bath solution, approximately 1.5 liters of plating bath solution were diluted with 400 gallons in Tank T-1. City water was used to dilute the plating solution for the first several runs because city water is used in the rinse tank. Water processed through the shop reverse osmosis unit (RO water) was used in later runs for dilution of the plating bath solution. After the tank was filled to the 400 gallon mark, the mixer was turned on to mix the contents of T-1. In addition, the process pump P-1 was turned on with full recirculation to T-1 for further mixing. After complete mixing, the valve positions were adjusted to pump the water through the ion exchange system. The average flow ranged from 300 to 700 ml/min. When the water level in the tank dropped below 100 gallons, the process pump was shut off and additional plating bath solution was added. The amount of solution added was calculated based on a 1000:1 dilution to bring the tank level back to 400 gallons.

Runs conducted using actual rinsewater were scheduled in advance to allow the chemical handlers to perform the transfer of the wastewater. When the water level in the tank dropped below 100 gallons, the chemical handlers were contacted again to transfer additional wastewater. The Shift Supervisor and Materials Manager were consulted in each case to ensure that the production schedule would not be affected.

A third set of runs was conducted which simulated final rinsewaters generated following a plating bath dragout. Approximately 60 gallons of RO water were spiked to about 1000 mg/L of Cd<sup>2+</sup> and processed through an ERU for 36 hours to reduce the Cd<sup>2+</sup> concentration. The resulting 60 gallons of water were transferred to T-1 and diluted to the 400 gallon mark using RO water. This tank of water was then processed through the ion exchange system.

At the conclusion of all test runs, any remaining wastewater was pumped to the CN-sump for transfer to the IWTP. A new batch of wastewater was then prepared for the next test run.

# 4.5.2 Preparation of Regeneration Solutions

10% Sulfuric Acid Solution - The Sulfuric Acid Chemical Feed Tank (T-3) was filled with approximately 25 gallons of city water. This was sufficient to conduct up to 15 regeneration sequences and to provide enough acid for cleaning glassware. A 10% by weight solution of H<sub>2</sub>SO<sub>4</sub> was prepared by adding approximately 1.6 gallons of 96% H<sub>2</sub>SO<sub>4</sub> to approximately 25 gallons of water. The contents of the tank were mixed and the specific gravity was then tested using a hydrometer. Acid or water was added until the specific gravity was approximately 1.07. Proper safety equipment was utilized including chemically resistant gloves, face shield, overalls and splash apron.

One of the objectives of the pilot system was to determine whether  $H_2SO_4$  could be reused once the  $Cd^2+$  had been removed in the electrolytic recovery unit. If any eluate  $H_2SO_4$  was available after using the ERU (T-4), it would be transferred into the Sulfuric Acid Chemical Feed Tank (T-3). The desired strength and volume would then be adjusted by adding fresh  $H_2SO_4$  or water until the specific gravity was approximately 1.07. No electrolytically recovered  $H_2SO_4$  was available, however, during the pilot plant runs.

5% Sodium Hydroxide Solution - The Sodium Hydroxide Chemical Feed Tank (T-2) was filled with approximately 25 gallons of city water. Approximately 3.7 gallons of sodium hydroxide (50%) was carefully added to the tank to prepare a 5% by weight solution of NaOH. The contents of the tank were mixed and the specific gravity of the contents of the tank was tested using a hydrometer. Additional NaOH or water was added until the specific gravity was approximately 1.05. Generally 25 to 30 gallons was sufficient for a three week period. Again, proper safety equipment was utilized while making up the solutions.

# 4.5.3 Loading Columns

Once the columns were assembled and mounted, they were filled and conditioned. The ion exchange resins were backwashed to remove any air pockets, resin fines, or other debris. The resins were then rinsed and regenerated according to the Regeneration Procedure outlined in the Test Plan.

Cation Resin - Approximately 1 hour prior to filling, the cation resin was placed in a container filled with water. Approximately 2 inches of glass beads were added to each cation column. The cation columns were then filled with approximately 10 inches of hydrated resin. The columns were backwashed using flexible hoses connected to the city water supply and discharged to the IWTP. The flow was maintained until all air pockets and particles were removed, and the bed was fully fluidized. A regeneration cycle was then conducted according to the regeneration procedure described in section 4.5.5.1 of this report.

Anion Resin - Approximately 1 hour prior to filling, the anion resin was placed in a container filled with water. Approximately 2 inches of glass beads were added to each anion column. The anion columns were then filled with approximately 12 inches of hydrated resin. The columns were backwashed using flexible hoses connected to the city water supply and discharged to the IWTP. The flow was maintained until all air pockets and particles were removed, and the bed was fully fluidized. A regeneration cycle was then conducted according to the regeneration procedure described in Section 4.5.5.2 of this report.

Activated Carbon - The activated carbon column was not utilized since there was no evidence that the Cd-CN plating tank had high concentrations of organic materials or brighteners in it.

# 4.5.4 System Operation

Once the wastewater batch in T-1 was fully mixed, the system was started. The columns to be operated were selected and the proper valve positions adjusted. The discharge from the process pump was then adjusted to recirculate the majority of the flow back to T-1 and the remaining desired flow to the ion exchange system. The pump discharge pressure and flow rate were checked periodically to ensure that the pressure drop across the filter had not exceeded 5 psi. Periodic samples were taken from T-1 to characterize the feed stream. Automatic ISCO® samplers were utilized to take hourly samples of the discharge from the lead cation and anion columns.

Samples were also taken from T-1 and the columns' discharge and analyzed using ion specific electrodes (ISE) and Hach® kit tests. This information was used to determine if the column had reached breakthrough. Breakthrough of the cation column was determined to occur when the concentration of Cd<sup>2+</sup> in the lead cation column effluent steadily increased and then leveled off. Full breakthrough occurs when the concentration in the influent is equal to the concentration in the effluent. When it was determined that a column had broken through, it was taken off-line for regeneration. If desired another column was put on-line.

Breakthrough of the anion column was determined to occur when the concentration of CN-in the effluent from the lead column steadily increased, and eventually became equal to that in the influent or until it leveled off. When breakthrough occurred, the column was taken off-line for regeneration and another column, if desired, was put on-line.

Utilizing the design basis, a test program was developed to incorporate the range of variables to be examined and their effect on the performance of the system. Table 4-2 outlines the proposed cation exchange runs to be conducted during the pilot system and are based on different regeneration flow rates. Table 4-3 outlines the proposed anion exchange runs.

Table 4-2: Proposed ion Exchange Test Run Matrix - Cation Columns

Total	Time.		N N N N N N N N N N N N N N N N N N N		2 2 2	===
	Ization		9 0 0	222	11 12 17	
	Neutralization		200	212	000	9001 9001 9001
	Rinse	SE .	% & & &	51.5	9 9 9 7 7 7	===
	Fest Rinse	ml/min	380	223	0 0 0	668 668 668 668 768 768 768 768 768 768
	- 1	2	0 0 0	0 <b>9</b>	# # # # # #	2 0 0 2 0 0 3 0 3
	Słow	mi/min t (mir	200 200 200	222	000	1000
		_	0 0 0 0 0	***	2 2 2	
	Regen	ml/min t (min	200 200 200	207	000	75 A B B B B B B B B B B B B B B B B B B
	Rinse	t (min)	000	222	500	5 0 0
	Initial	ml/min t	9 8 8 9 8 0 0 8 0	980	3 80 0 80 0 80	00 0 0 00 0 0 00 0 0
	2	ml/min Cd(mg/l)	6 6 6 6 8 8	222	8 8 8 8 8 8	23 23 23
olumns	Peed.	ml/min	360 360 380	0.000	0 0 0 0 0 0 0 0 0	000
Cation Columns		Run #	1-20	0000 4000 9000	3-10 3-20 3-30	000

Source: Arthur D. Little, Inc.

Table 4-3: Proposed ion Exchange Test Run Matrix - Anion Columns

Total	Time		1 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	===	133 133 133	===
	Rinse		N N N Ø Ø Ø	333	N N N B B B	:::
	Fast Rinse	)   	38 38 38 30 30 30 30 30 30 30 30 30 30 30 30 30		0 8 8 0 0 8 0 0 8 0	
	Rinse	t (min)	<b>444</b>		N N N N N N	
	Slow Ri	ml/min	600 600 600	998	1000	200
	eration	t (min)	900		8 8 8 0 0	
	Regen	ml/min t (mi	800 800 800	233	1000	3 2 3
	Rinse	t (min)	0 0 0	20 20 20 20 20 20 20 20 20 20 20 20 20 2	20 20 20	222
	Initial	ml/min	380 380 080	222	380	
	72	min Cd(mg/l)	8 8 8 8 8 8	200	2333	222
kumus skumus	Ţ	ml/min	380 380 380	222	380 380	223
Anion Columns		Run #	1-1A 1-2A 1-3A	* * * \$	3-1A 3-2A 3-3A	445 445 443

The ISE probes were calibrated on a daily basis. The liquid level in all the process tanks and chemical storage tanks was inspected daily to prevent any overfilling.

## 4.5.5 Regeneration

Once a column exhibited full breakthrough, it was taken off-line to be regenerated. Regeneration consists of several steps: (1) initial rinsing, (2) chemical regeneration, and (3) final rinsing. The cation resin has an additional neutralization step to return the resin to its sodium form before the final rinse step. The chemical regeneration and rinsing steps are conducted in a "downflow" mode to prevent the resin bed from expanding. The process fluid enters the top of the column and exits at the bottom of the column. Table 4-4 shows the operating parameters chosen for the regeneration of the cation and anion columns.

4.5.5.1 Cation Column Regeneration. The procedure followed for regeneration of the carion columns is outlined below.

#### Initial Rinse

The city water supply was connected to the top of the column and the discharge hose was directed to the CN- sump. A city water rinse was conducted for approximately 1 hour to remove any CN- in the column. Approximately 18 bed volumes (BV) were processed.

# Chemical Regeneration

The discharge from the Sulfuric Acid Pump (P-5) was connected to the top of the column and the discharge directed to the Dilute Sulfuric Acid Tank (T-5). The portable mixer in the Sulfuric Acid Feed Tank (T-3) was turned on to agitate the contents of the tank. The flow rate of the H<sub>2</sub>SO<sub>4</sub> solution was adjusted to 200 to 1,000 ml/min. This rate was a variable and was changed for several regeneration runs to determine the optimum rate to achieve a sharp bell curve. The pH and volume throughput was monitored to determine when the acid broke through the column. When the pH dropped below 2, the sulfuric acid pump was shut off. This resulted in approximately 1.8 BV of throughput.

#### Rinse

A slow rinse was conducted using city water. The flow rate was adjusted to approximately the same flow rate as the acid regeneration step. The slow rinse step displaced the acid within the column. Approximately 3 BV were required. The slow rinse was discharged to the Concentrated Eluate Tank (T-6). After the pH had stabilized above 0, the slow rinse was stopped.

# Table 4-4: Ion Exchange Regeneration Parameters

Parameter	Value
Cation Columns	
Initial Rinse Flow Rate	0.38 L/min
	3.5 L
Initial Rinse Volume	***
Regeneration Flow Rate	0.04 - 0.08 L/min
	6-12 lbs H <sub>2</sub> SO <sub>4</sub> / ft <sup>3</sup>
Acid Requirement	1.87 L 10% H <sub>2</sub> SO <sub>4</sub> solution
Volume of Regenerant	
Slow Rinse Flow Rate	0.04 - 0.08 L/min
Slow Rinse Volume	1.2
<del></del>	0.38 L/min
Fast Rinse Flow Rate	10.5 L
Fast Rinse Volume	
N Name of Flow Bots	0.04 - 0.08 L/min
Neutralization Flow Rate	4 lbs NaOH/ ft3
NaOH Requirement	1.32 L 5% NaOH solution
Volume of Neutralization Solution	
The Line Flow Para	0.38 L/min
Final Rinse Flow Rate	2.5 L
Final Rinse Volume	
Anion Columns	
	0.38 L/min
Initial Rinse Flow Rate	7.4 L
Initial Rinse Volume	=
Town Bate	0.08 - 0.16 L/min
Regeneration Flow Rate	4 lbs NaOH/ ft <sup>3</sup>
NaOH Requirement	3 L
Volume of Regenerant	<del>-</del>
Slow Rinse Flow Rate	0.08 - 0.17 L/min
	2.5 L
Slow Rinse Volume	0.38 L/min
Fast Rinse Flow Rate	22 L
Fast Rinse Volume	<del></del>

The next rinse, the fast rinse, removed any remaining sulfuric acid. The fast rinse was conducted using city water at a flow rate approximately equal to the wastewater processing rate. The fast rinse was discharged to the dilute sulfuric acid tank T-5. When the pH had stabilized at about 2, the fast rinse was stopped. The usual volume throughput was 14 BV.

#### Neutralization

The discharge from the Sodium Hydroxide Pump (P-6) was connected to the top of the column. The discharge from the column was directed to the spare tank T-8. The mixer in the Sodium Hydroxide Tank (T-2) was turned on to agitate the sodium hydroxide solution. The flow rate of NaOH was adjusted to 200 to 1,000 ml/min (the same as the regeneration rate), and allowed to run until the pH rose to above 11. The neutralization step was then stopped after approximately 2 BV were processed.

#### Rinse

The final rinse was essentially a repeat of the fast rinse conducted after the chemical regeneration step but was intended to remove any remaining NaOH in the column. City water was used at a flow rate approximately equal to the wastewater processing flow rate. When the pH had stabilized at approximately 12, the rinse was stopped and the regeneration sequence was complete. The required rinsewater volume for this step was approximately 14 BV.

4.5.5.2 Anion Column Regeneration. The procedure followed for anion column regeneration is outlined below.

#### Initial Rinse

The city water supply was connected to the top of the column and the discharge hose was directed to the CN- sump. A city water rinse was conducted for approximately 20 minutes to remove any residual process water in the column utilizing 10 BV.

#### Chemical Regeneration

The discharge from the Sodium Hydroxide Pump (P-6) was connected to the top of the column and the discharge directed to the Sodium CN- Eluate Tank (T-7). The portable mixer in the Sodium Hydroxide Tank (T-2) was turned on to agitate the contents of the tank. The flow rate of the NaOH solution was adjusted to 200 to 1,000 ml/min. This rate was a variable and was changed for several regeneration runs to determine the optimum rate to achieve a sharp bell curve. The pH and volume throughput was monitored to determine when the NaOH was breaking through the column. When the pH rose above 12, the sodium hydroxide pump was shut off. This occurred after processing approximately 2 BV.

#### Rinse

A slow rinse was conducted using city water. The flow rate was adjusted to approximately the same flow rate as the sodium hydroxide regeneration step. The slow rinse step displaced the sodium hydroxide within the column. The slow rinse was discharged to the Sodium CN- Eluate Tank (T-7). After the pH had stabilized below 13, the slow rinse was stopped. This required approximately 2 BV.

The next rinse, the fast rinse, removed any remaining sodium hydroxide. The fast rinse was conducted using city water at a flow rate approximately equal to the wastewater processing rate. The fast rinse was discharged to the Sodium CN- Eluate Tank (T-7). When the pH had stabilized at about 12, the fast rinse was stopped and the regeneration procedure was complete, usually after 7 to 8 BV.

## 4.6 Sampling Procedures

The frequency with which sampling occurred, and the location where samples were drawn is presented in Appendix A. The samples from the column effluent were primarily taken using ISCO® samplers programmed to draw a sample once per hour. Not all of these samples were submitted to the laboratory for analysis. Approximately every third sample was submitted.

A sample was drawn from the feed tank T-1 for each new batch that was made up and analyzed for a full cation and anion characterization. In addition, a daily sample was taken to determine if the CN-concentration was decreasing.

Two sampling procedures were used during regeneration. The first procedure called for sampling every 5 to 10 minutes while allowing the remainder of the flow to go to its proper discharge point. This procedure was used to determine the volume and timing for directing the eluate solution to the electrolytic recovery cell.

The second sampling procedure was utilized to develop material balances. In these runs, all of the eluate volume was collected in a series of one-liter bottles. A representative sample of these one-liter bottles was collected and analyzed for Cd<sup>2+</sup> and CN-concentration, and the time interval over which they were collected was recorded. This allowed the percent Cd<sup>2+</sup> and CN-recovery to be accurately calculated.

Samples were taken from the ERU overflow line to measure the reduction in Cd<sup>2+</sup> concentration over time. During the CN- based run, additional samples were taken to determine if the electrolytic process enhanced the oxidative degradation of CN-.

To allow for the identification of the samples, each bottle was labeled after the sample had been drawn. The labeling information included the date, sample number, and time when

the sample was drawn. The sample numbers were assigned sequentially and sample information was entered into the sampling log book.

Samples were periodically taken and analyzed with portable ISEs and Hach® kits. For the cation columns, the ISE for cadmium detection could not be used because the Cd-CN complex could not be measured with the probe. A Hach® kit was used to detect the level of Cd²+ in the column discharge. Cyanide ISEs were also used for measuring the level of CN- in the column effluent. The CN- probes were concentration-limited in that the electrode would be consumed in concentrations in excess of 10 mg/l. Thus, any samples above this concentration required dilutions. A Hach® kit was also used to measure CN- and for sample verification. Photograph 4-4 shows the on-site analytical setup for the program.

Both the CN- and Cd<sup>2+</sup> Hach kits were colorimetric and required large dilutions (100 to 1000:1) to bring the sample into the correct colorimetric range. Because of these large dilutions, the results of these kits were used for engineering control only.

In order to measure pH, pH probes were used. These probes worked well in all applications.

Photograph 4-4. On-Site Analytical Setup for Cd<sup>2+</sup> and CN<sup>-</sup> Analysis



## 5.1 Summary of Results

The objective of the Cd-CN wastewater treatment pilot test program was to determine the feasibility of cation/anion exchange and electrolytic recovery for the treatment and recycle of Cd and CN- from actual plating rinsewater. The optimum conditions for operating the ion exchange system, observed during the laboratory phase of this study, were utilized during the pilot test program to gather insight into resin capacity, optimum regeneration conditions, process safety issues, process monitoring, emergency procedures and the performance of on-line instrumentation. In addition, the pilot study was more specifically focused on determining the ability of the cation/anion exchange system to treat the plating rinsewater at NADEP North Island. To investigate the ion exchange systems' applicability to North Island, four different types of cadmium plating rinsewater were processed, including:

- City water with low concentrations of Cd<sup>2+</sup> and CN-:
- City water with high concentrations of Cd<sup>2+</sup> and CN- (actual rinsewater);
- RO water with low concentrations of Cd<sup>2+</sup> and CN-; and
- RO water treated by an electrolytic recovery unit.

Cadmium Resin Capacities. The cation exchange system proved to be technically capable of breaking the Cd-CN complex and removing and concentrating Cd<sup>2+</sup> from all four of the plating rinsewaters. The Cd<sup>2+</sup> resin capacities from pilot operations were found to be similar to the results found in the laboratory ion exchange study; varying from 75 meq/L for Run BC-2 (a city water run with low Cd<sup>2+</sup> concentration and a high cation concentration) to 630 meq/L for Run BC-9 (a RO water run with a low Cd<sup>2+</sup> concentration and a very low ionic strength). The pilot testing also demonstrated the same relationship between non-Cd<sup>2+</sup> cation concentration and Cd<sup>2+</sup> concentration and Cd<sup>2+</sup> resin capacity as observed in the laboratory study:

- Cd<sup>2+</sup> resin capacity increases as the non-Cd<sup>2+</sup> cation concentration of the solution decreases (at a constant non-Cd<sup>2+</sup> cation: Cd<sup>2+</sup> molar ratio); and
- Cd<sup>2+</sup> resin capacity increases as the molar ratio of non-Cd<sup>2+</sup> cations:Cd decreases.

The capacity of the resin for Cd<sup>2+</sup>, as predicted by the laboratory results, was shown to be affected by the cation concentration of the water being used in the plating rinse tank. The city water at NADEP North Island contains high concentrations of dissolved solids such as calcium, magnesium, and sodium which decreased the resin's capacity for Cd<sup>2+</sup>. The results showed an average Cd<sup>2+</sup> resin capacity of 150 meq/L for the city water runs with low Cd<sup>2+</sup> concentration; an average Cd<sup>2+</sup> resin capacity of 430 meq/L for the city water runs with a high Cd<sup>2+</sup> concentration; an average Cd<sup>2+</sup> resin capacity of 480

meq/L for the RO water runs; and a Cd<sup>2+</sup> resin capacity of 410 meq/L for the electrolytically treated dragout water.

The first set of city water runs, with a low Cd<sup>2+</sup> concentration, had the lowest Cd<sup>2+</sup> resin capacity because these runs on average had the highest cation concentration and the highest cation:Cd molar ratio. The second set of city water runs, with a high Cd<sup>2+</sup> concentration, had much higher Cd<sup>2+</sup> resin capacity even though the cation concentration remained constant because the cation:Cd molar ratio decreased from 60 to 30 (due to the higher Cd<sup>2+</sup> concentration). The RO water runs had a slightly better Cd<sup>2+</sup> resin capacity than the second set of city water runs because the cation concentration of the RO water runs was much lower than the city water runs; therefore, the cation:Cd molar ratio was lower, 25. The results of these three sets of runs supports the general conclusion that the Cd<sup>2+</sup> resin capacity increases as a function of the decrease in the cation concentration and the cation:Cd molar ratio.

However in contrast to the two sets of city water runs and the RO water runs, the electrolytically treated dragout water run did not correlate with the predicted results of the laboratory model. The model predicted a Cd<sup>2+</sup> resin capacity of 170 meq/L and the actual pilot plant result was 410 meq/L. The reason for the difference between the predicted and actual results is unknown.

Cation Regeneration. The regeneration of the cation columns was performed at several different flow rates over a range of 0.5 BV/hr to 5.0 BV/hr. The lower regeneration flow rates resulted in a more concentrated cadmium sulfate (CdSO<sub>4</sub>) solution eluting from the column in a smaller number of bed volumes. For a flow rate of 1.1 BV/hr and 2.2 BV/hr, the CdSO<sub>4</sub> was collected between 1.5 and 2.5 bed volumes. In addition, a flow rate of 2.2 BV/hr or less appeared to minimize leakage of Cd<sup>2+</sup> from freshly regenerated polishing columns.

The apparent recovery during regeneration ranged from 67% to 157% but averaged at nearly 100%. The concentrated portion of the regenerant stream was collected for processing in an electrolytic recovery unit (ERU) to recover the Cd<sup>2+</sup> as Cd metal. The average concentration of the eluate was approximately 1200 mg/L and included several thousand mg/L of other cations, including Na+, Ca<sup>2+</sup>, and Mg<sup>2+</sup>.

The concentrated regenerant, CdSO<sub>4</sub>, was collected and processed through an ERU for recovery of Cd metal. Approximately 97% of the cadmium was recovered from the solution as Cd metal, however, the quality of the plate was poor. The quality of the plate was affected by the high current density applied, the slow agitation rate, and the extremely low pH of the solution. The calculated current efficiency was very low, 22%, indicating that almost all of the current went to forming hydrogen gas. It is likely that the recovered cadmium could be reused in the plating tank (in the anode bags) or the vacuum cadmium system if the quality of the plate were improved. To improve the

efficiency and quality of the plate, process conditions would need to be altered to raise the pH and increase the agitation.

Cyanide Resin Capacities. The recovery and reuse of CN- from the plating rinsewater using an anion exchange resin was not an efficient recovery technology and was eliminated from the full-scale design for two reasons:

- The high concentration of non-CN-anions (e.g., CO<sub>3</sub><sup>2</sup>-, SO<sub>4</sub><sup>2</sup>-, Cl-) present in both the city water and the plating solution had a strong negative impact on the CN-resin capacity.
- The low affinity of the anion resin for CN- produced a breakthrough curve where CN- quickly broke through the resin bed at the regulatory limit (within the first 20 bed volumes) and then slowly reached complete breakthrough.

Because of the high concentration of anions in the rinsewater, the OH-CN resin capacity model developed in the laboratory study was invalidated and could not be used to predict the actual CN- breakthrough. While the model was not able to predict the actual CN- resin capacity, the results did show that as the concentration of cyanide decreased the resin CN- capacity decreased as demonstrated in the laboratory study. The anion columns had an average capacity of 140 meq/L when using city water. The capacity was slightly increased to an average of 190 meq/L when utilizing RO water; however, this is still only 15% of the manufacturer's estimate of total resin capacity. The average CN- resin capacity for the electrolytically treated dragout water (RO D.O.) was 450 meq/L. This higher capacity is attributed to the higher CN- solution concentration, 180 mg/L. The total anion concentration: CN- ratio for these runs and the RO water runs are identical, indicating that CN- solution concentration has more of an effect on CN- resin capacity than does total anion concentration.

As mentioned above, the low affinity of the anion resin for CN- produced a breakthrough curve where CN- quickly broke through the resin bed at the regulatory limit and then slowly reached complete breakthrough. The swift breakthrough caused the polishing column to also reach the regulatory breakthrough rapidly; therefore, the anion columns were quickly out of compliance with the Federal Pretreatment Standards for Metal Finishers (compliance limit of 1.2 mg/L Total Cyanide [TCN] daily maximum and 0.65 mg/L average monthly for existing systems<sup>10</sup>). The effluent from the polishing column was unable to maintain this compliance level for more than a few hours after being put on-line. In order to maintain compliance for even a complete day the volume of anion resin would have to be increased by a factor of at least 10.

Anion Regeneration. Regeneration of the anion columns indicated poor recovery of the CN-. Recovery of CN- ranged from 12 to 15%, and the concentration of CN- in the solution was approximately 650 mg/L which is far below the plating bath concentration of 25,000 to 30,000 mg/L. In addition, the anions (e.g., Cl-, CO<sub>3</sub><sup>2</sup>-, SO<sub>4</sub><sup>2</sup>-) which

compete with the CN- for removal by the anion resin are also removed during regeneration (some of which are considered contaminants to the plating bath). The CN-was also noted to degrade in the feed tank of the ion exchange system into cyanates (CNO-) which are also plating bath contaminants. Thus the low concentration of CN-and the presence of plating bath contaminants, make the reuse of the anion eluate in the plating bath impossible without additional processing.

Because the CN-solution cannot be reused directly in the plating bath and the anion columns are not reliable for maintaining compliance with the regulatory limits, the use of ion exchange for the treatment of CN- was not included in the preliminary design. Instead, conventional alkaline chlorination was the assumed method for treating the CN-contaminated streams exiting the cation columns.

# 5.2 Column Breakthrough and Resin Capacity

Approximately 13 cation runs (Table 5-1) and 7 anion runs (Table 5-2) were conducted to develop cation and anion breakthrough curves. Four types of wastewater were processed through the columns to determine: their effect on Cd<sup>2+</sup> and CN- resin capacity; and the ability of the ion exchange system to meet regulatory limits for the different rinsewaters that North Island might have to treat, including:

- City water with a Cd<sup>2+</sup> concentration of approximately 22 mg/L and a CN-concentration of 58 mg/L. These runs were conducted to demonstrate the ability of the cation/anion exchange system to treat actual plating rinsewater based on the operation of the rinse tanks prior to the installation of the pilot system;
- City water with a Cd<sup>2+</sup> concentration of approximately 76 mg/L and a CN-concentration of 77 mg/L. These runs were conducted to demonstrate the ability of the cation/anion exchange system to treat actual plating rinsewater based on the operation of the rinse tanks after North Island reduced the volume of plating rinsewater generated by holding the rinsewater longer in the rinse tanks. These runs were not performed using the anion columns because of the low CN-resin capacities and the short time to reach breakthrough at the regulatory limit observed in earlier runs;
- Reverse osmosis (RO) water with a Cd<sup>2+</sup> concentration of approximately 28 mg/L and a CN-concentration of 48 mg/L. These runs were conducted to demonstrate the ability of the cation/anion exchange system to treat actual plating rinsewater if the overall cation concentration of the plating rinsewater were to be reduced by using RO water instead of city water, and
- Electrolytically treated dragout water with a Cd<sup>2+</sup> concentration of approximately 50 mg/L and a CN- concentration of 180 mg/L. This run simulated the treatment of

Table 5-1: Summary of Pilot Test Runs for Cation Columns

<u> </u>				<del></del>													
<b>2</b> 2 2 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	4/1/82	4/1/82	4/16/92	4/16/92	4/16/92	5/15/92	5/14/82	5/16/92	6/11/92	6/12/92	6/15/02	6/20/92	6/24/92	6/24/92	6/25/92	7/22/02	7/23/92
Cotumn	5	2-2	5	C-2	C-3	5	င်း	25	5	C-2	ទី	5	C-2	ပိ	5	5	25
Pagen Plum Number	RC-1	RC-2	RC3	AC.4	RC-S	RC 6	AC-7	AC.	RC.9	AC-10	RC-11	RC-12	AC-13	RC-14	RC-15	AC-16	RC-17
Total Mines Weier Treeted (L)	140		790		480	099	200		1000	1100		2100	3000	480	1400	1100	006
Run Duration (hours)	12		\$		•	*	2	-	2	\$		8	2	12	32	\$	<b>5.8</b>
Frow Rate (mYmdn)	200		300		200	8	904		980	370		230	82	700	780	430	920
Įį	4/8/92		4/13/82		4/15/92	5/12/92	5/13/92		6/8/92	6/10/92		6/15/92	6/16/92	6/23/92	6/24/92	7/20/92	7/22/92
Polishing Column	C-2		25		1	ន	3		<b>62</b>	ຮ		2-5	ខ	l	l	I	
Column	<u>ن</u> 1.3	-	ទី		3	2	ខ្ល		ទ	C-2		2	<del>د</del> د	C-3	<del>ن</del>	<u>د</u>	C-2
Froms Water Type (a)	CW Low Cd		CW Low Cd		CW Low Cd	CW Low Cd	CW Low Cd		CW Low Cd	CW Low Cd		RO Water	RO Water	RO Water	RO (0.0.)	CW High Cd	CW High Cd
	BC-1		BC-2		803	<b>8</b> C4	80-5		<b>8</b> 28	<b>8</b> C7		8-58	<b>8</b> 0	BC-10	BC-11	BC-12	BC-13

CW Low Cd - City water low Cd2+ concentration
RO Water - Reverse Gemosis Water
RO (0.0.) - Electrolytically treated dragout water
CW High Cd - City water with high Cd2+ concentration (actual rinsewater) 3

Table 5-2: Summary of Pilot Test Runs for Anion Columns

				·						
11	4/13/92	4/13/92	4/15/92	4/15/92	4/16/92	6/18/92	6/16/92	6/23/92	6/25/92	6/26/92
Cobean	A-1	A-2	A-1	A-2	A-3	A-1	A-2	A-1	A-1	A-2
	PA-1	RA-2	RA-3	RA	RA-6	<b>8</b> 46	PA-7	PA-8	RA-9	RA-10
The Paris Water Transic CD	140		986		430	1200		750	950	490
Run Dutation (hours)	12		8		22	8		12	*	•
Flow Rate (milmin)	200		86		900	009		750	2,9	1080
Start Dese	26/9/5		4/13/92		4/14/92	6/15/82		6/20/92	6/24/92	8/25/92
Polishing Column	A-2		A-2		1	A-2			ı	,
Lasd Columb	A-1		A-1		A-3	A-1		A-1	<b>A-1</b>	A-2
Process Wester Type (s)	CW LOW CN-		CW Low CN		CW LOW CN-	RO Water		RO Water	RO (DO)	RO (00)
Pan Number	BA-1		BA-2		BA-3	844		84.6	BA-6	BA-7

(a) CW Low CN- - City water low CN- concentration RO water - Reverse Cemosis Water RO (D.O.) - Electrolytically treated dragout water

Source: Arthur D. Little, Inc.

the plating rinsewater by an electrolytic recovery unit (ERU) followed by treatment by ion exchange to remove the remaining Cd<sup>2+</sup> and CN<sup>-</sup>.

Table 5-3 presents the characterization of the four plating rinsewaters processed through the system. The city water has a higher concentration of cation and anion species than the RO water. These additional ions compete with the Cd<sup>2+</sup> and CN- ions for removal on the resin, and affect the resin's capacity. The actual rinsewater had a higher average Cd<sup>2+</sup> and CN- concentration because during the pilot test program, the plating rinsewater handling procedures were changed at the North Island facility to eliminate discharges from the Cd<sup>2+</sup> rinse tank to the IWTP. Because the plating rinsewater was no longer discharged to the IWTP, the volume of rinsewater generated by the facility was reduced by holding the water in the plating rinse tank for longer periods of time. In some samples, the total anion and cation concentrations are not equivalent. This is due to an additional anion or cation species which is present in the water but was not analyzed for such as nitrate (NO<sub>3</sub>-) or potassium (K+)

Breakthrough curves were developed for both the cation and anion columns for these four different rinsewaters to determine the capacity of the resin to remove either Cd<sup>2+</sup> or CN<sup>-</sup>. These curves were developed by plotting the contaminant concentration in the column effluent versus throughput volume (bed volume). When the concentration of the material entering the column was equal to the concentration leaving, the column was considered to have reached complete breakthrough. In some cases, complete breakthrough never reached the inlet concentration, but was determined to occur when the effluent had leveled off at a constant concentration (see Section 5.2.1.3, Operational Difficulties). The breakthrough curves were also used to determine the regulatory breakthrough, which was the point where the effluent contaminant concentration exceeded the daily maximum regulatory limit.

Cyanide and cadmium resin capacities were calculated graphically from the area to the left of the breakthrough curve bounded by the y axis, the breakthrough curve, and the feed concentration. For those runs where complete breakthrough was not reached the breakthrough curve was extrapolated to estimate the point at which complete breakthrough would have occurred, to allow an estimated capacity to be calculated.

The complete breakthrough volume in BV's for the lead column is reported as the volume of water processed through the column until the Cd<sup>2+</sup> concentration in the effluent reaches the feed concentration. The complete-breakthrough volume in BV's for the polishing columns (BC-7, BC-9, and BC-13) is reported as equivalent BV's of feed. The equivalent BVs of feed is a calculated value that is derived from the total mass of Cd<sup>2+</sup> removed by the resin on the polishing column. The mass of Cd<sup>2+</sup> removed in milligrams, as calculated by the previously described graphical method, is divided by the average feed concentration (mg/L) resulting in the equivalent number of BV of wastewater at the feed concentration that the polishing column processed. This normalizes the complete breakthrough volume of the polishing columns, since for much

Table 5-3: Rinsewater Characterization Data

## Car Total Data    Talk   Car Total Data			7.3						Comp	Sonoentration (mg/L)	n (mg/L							
######################################	Sampla Location	Par Nation	£3	8	3 3	3 %	2	8	3			8	8	ğ	8		153	
Control   Cont	City Water RO Water		1 1	1 1	오 1	1 1	5 2	8 S	% ⊋	]		2.00	2 8	8 8	≗ ¤	<b>!</b>		4
80-5 80-5 80-5 80-5 80-5 80-5 80-5 80-5	Pating Rinsewater Tank T-1 (CW low Cd)	7 7 7 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	182215	285858	C = 2 = 2 = 2	111111	8 <b>28</b> 1 1 1	721115	211178			52111S	881115	821115	351113			221115
Color		8 8 0 0 8 8	0 0	8 4 8	2 2	1 1	1 1	2	<b>;</b> 1 1			<b>?</b>   1	<b>8</b> 1 1	<b>i</b> i	1 1			
BC-7		<b>3</b> 3 5	213	8=4	18 <b>%</b> N	811	<b>2</b> 11	RII	211			<b>3</b> 11	<b>2</b> 11	211	211			
90-7		주 7. 7	1 6	88	88	22	18	। %	1 %				1 ‰	े । क्ष	.   <b>8</b>			
### 100   Fig. 100   F		BC-7	7.0	8	8	1	١	1	1				1	1	1			
9C-6 BA-6       1       52       32       10         9C-6       104       51       33       1       1         9C-6       104       51       33       1       1       1         9C-6       104       51       34       50       52       10         9C-6       105       52       27       1       1       1       1       1         9C-6       107       52       28       1       121       NO       NO       0.3       2.4       80       2.1       97         9C-6       107       52       28       1       121       NO       NO       0.3       2.4       80       2.1       97         9C-6       107       52       28       1       121       NO       NO       0.3       2.4       80       2.1       9.7       2.9       80       80       1.0	T-1 (RO Water)	14 60 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	10.5 10.7	84	<b>3</b> R :	11	<b>2</b> 1	21	<b>3</b> 1			<b>9</b> 1	<b>2</b> 1	21	<b>R</b> 1	See See See	•	- Arts (***)
80-9 10.4 51 31			1 1	8 3	, 8	1 1	1 2	1 2	1 2			19	। ह्र	32	1 =			15
90.4		<b>8</b>	10.4	5	ਙ	ł	1	ı	1				ı	1	1			
BC-9		ខ្លួន	1 8	8.3	t R	1 1	18	1 2	12			1 3	18	1 2	Į			
BC-9, BA-5 10.7 52 29 - 121 NO NO 0.3 2.3 97 2.9 88 C-9 - 37 39 - 121 NO NO 0.3 2.3 97 2.9 88 C-9 - 37 39 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -		9 2	1	8	72	1	124	£	Ş			3	8	2	6	_		
80-9		BC-9, BA-5	10.7	25	8	Į	121	2	웆			<b>6</b>	6	20	8			
80-40		8C-8	1	31	8	1	1	1	1 3		1	j *	1 2		1		á	
BC-11, BA-6 11 146 51 51 416 NO NO 1.0 10 302 7.8 301 BC-11, BA-7 10.0 210 48 — — — — — — — — — — — — — — — — — —		Ž.	1 1	1	<b>%</b> 8	1 1	<b>3</b> 1	2 1	2 1	**		<b>3</b> 1	<b>Ž</b> 1	<b>3</b> 1	<b>8</b> 1			100
BC-11, BA-7 10.9 210 48 — — — — 1.0 1.0 1.0 1.0 1.7 1.0 1.0 1.7 1.0 1.0 1.7 1.0 1.0 1.7 1.0 1.0 1.7 1.0 1.0 1.7 1.0 1.0 1.0 1.7 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	T.1 (BO IDON	BC-11 BA-6	=	ੂ <b>3</b>	, 2	2	1	ş	2				¥	7.8	8			
90 SC-12		BC-11, BA-7	10.0	210	\$	1	1	ı	1			i	1	ł	1			
8C-12 9.8 88 88 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	T-1 (CW high Cd) -	80-12	3	K	8	3	8	*	2			2	2	2	12	: -		4.3
9.8 83 87 88 88 88 88 88 88 88 88 88 88 88 88	(actual rinsewater)	\$0.12 80.12	1	8	R	R	1	1	1			1	1	1	1	. 😿		
9.9 83 67 65 333 10 22 0.9 5.4 - 214		BC-13		2	8	8	1	1	1			1	1	1	1	-		7.5
		BC-13	8.8	8	6	<b>S</b>	g	2	8			7	ı	2		_	_	

Not analyzed for ND - Not Detected
Shaded and unshaded areas indicate new wastewater batches

of the time it is loaded gradually with Cd<sup>2+</sup> from the effluent of the lead column; whereas the lead column is loaded at the constant feed concentration.

Appendix B includes the breakthrough curves for each of the 13 Cd<sup>2+</sup> breakthrough runs except BC-1. The breakthrough curve for run BC-1 is not included because insufficient samples were collected during this initial run to plot a breakthrough curve. In addition, complete breakthrough was not reached for runs BC-3, BC-4, BC-5, and BC-8 because the field data used to determine when breakthrough was occurring were not accurate (see Section 5.2.1.3, Operational Problems); thus the columns were taken off-line prematurely. These runs do, however, provide indications of leakage of Cd<sup>2+</sup> from the polishing column and regulatory breakthrough. Runs BC-10 and BC-11 did not reach full breakthrough because there was not a sufficient amount of water in T-1 to continue operation of the system.

#### 5.2.1 Cation Column Results

Table 5-4 summarizes the cation runs conducted during the seven-week pilot plant operation. The objective of conducting the runs with different types of plating rinsewaters was to:

- Evaluate Cd<sup>2+</sup> resin capacity at different Cd<sup>2+</sup> and cation concentrations;
- Evaluate the ability of the laboratory model to accurately predict Cd<sup>2+</sup> resin capacity:
- Evaluate the use of ion exchange to treat different types of actual plating rinsewater generated from North Island plating operations;
- Evaluate the use of ion exchange for Cd<sup>2+</sup> removal and recovery from dragout solutions processed in an electrolytic recovery unit;
- Evaluate compliance with regulatory limits; and
- Identify both actual and potential operational problems.

**5.2.1.1 Cadmlum Resin Capacity.** The Cd<sup>2+</sup> resin capacities (Table 5-4) from pilot test operations were found to be similar to the results found in the laboratory ion exchange study; resin capacities varied from 75 meq/L for Run BC-2 (a city water run with low Cd<sup>2+</sup> concentration and a high cation concentration) to 630 meq/L for Run BC-9 (a RO water run with a low Cd<sup>2+</sup> concentration and a very low cation concentration).

The Cd<sup>2+</sup> resin capacities calculated in the pilot tests demonstrated the same relationship between cation concentration and Cd<sup>2+</sup> concentration to Cd<sup>2+</sup> resin capacity as observed in the laboratory study:

Table 5-4: Summary of Cation Column Capacity

Processes   Lanel   Cole   C					Pas C	Intestritection		Catuma By	pecification		Cetton Column P	plumen Peduale	
CW bw Cd C-1 is 14 87 200 12 10 — — — — — — — — — — — — — — — — — —		įį	3	8	<b>§</b>	CodentCd Moler Rode	Flore Flats	Bed Vetame		Actual Col	Predicted Cd Capacity	Complete BreakStrough	Professory Professory Professory
CW bwy Cd				Type:	(Treat)		(me/meln)	TO TO	(BVA)	(mea/L)	· (meq.)	(By	<b>6</b>
21         14         87         300         12         15         75         135           22         14         75         800         12         22         11         —         —           22         12         75         400         22         11         —         —           23         16         62         360         22         11         —         —           30         15         62         300         22         10         140         170           22         14         72         361         1,8         13         146         170           23         6,1         24         700         22         14         340         472           24         700         22         14         340         472           25         6,1         24         700         22         19         —         —           26         17         70         22         19         485         451           27         430         22         12         420         170           26         17         22         12         420         27 <td>Š</td> <td>CW low Cd</td> <td>2</td> <td>:</td> <td>:</td> <th>20</th> <td>200</td> <td>1.2</td> <td>0</td> <td></td> <td>1</td> <td>-</td> <td>1</td>	Š	CW low Cd	2	:	:	20	200	1.2	0		1	-	1
CW low Cd C-3	20%	CW low Cd	3		2	26	300	12	<b>\$</b>	2	85	82	150
CW low Cd   C-1   22   12   61   400   22   11         CW low Cd   C-3   19   12   75   400   22   11         CW low Cd   C-1   29   16   62   360   22   10   140   170     CW low Cd   C-2   30   15   56   370   22   10   230   230     CW low Cd   C-2   30   15   56   370   22   10   230   230     FO Waler Ann with Low Cd   22   61   24   700   22   14   340   430     FO Waler Ann with Low Cd   29   61   24   700   22   19   630   472     FO Waler Ann with Low Cd   29   61   24   700   22   19   640   430     FO (D.O.)   C-1   69   17   28   430   22   18   465   451     CW high Cd   C-1   69   17   28   430   22   18   620   270     CW high Cd   C-2   60   16   27   480   22   15   620   330     CW high Cd   C-2   60   16   27   480   22   15   625   330     CW high Cd   C-2   60   16   27   480   22   15   425   300     CW high Cd   C-2   60   16   27   480   22   15   425   300     CW high Cd   C-2   60   16   27   480   22   15   425   300     CW high Cd   C-2   60   16   27   480   22   15   425   300     CW high Cd   C-2   60   16   27   480   22   15   425   300     CW high Cd   C-2   60   16   27   480   22   15   425   300     CW high Cd   C-2   60   16   27   480   22   15   425   300     CW high Cd   C-2   60   16   60   60   60   60   60     CW high Cd   C-2   60   16   60   60   60   60   60     CW high Cd   C-2   60   16   60   60   60   60   60   60	200	CW low Cd	3	8	=	75	8	12	83	ı	l	ł	160
CW low Cd         C-3         16         12         75         400         22         11         —         —           CW low Cd         C-1         29         16         62         360         22         10         140         170           CW low Cd         C-2         30         15         56         370         22         10         230         230           FO Waler Anna Min Low Cd         22         14         72         361         1,8         13         146         178           FO Waler         C-1         29         6.1         24         530         22         14         340         430           FO Waler         C-2         28         6.1         24         700         22         19         425         472           FO Waler         C-3         29         6.1         24         700         22         19         465         451           FO (D.O.)         C-1         60         17         24         400         22         19         465         451           FO (D.O.)         C-1         60         17         28         430         22         12         465         30	7	CW low Cd	5	n	ğ	5	904	2.2	=	j	ı	ł	052
CW low Cd         C-1         29         16         62         300         22         10         140         170           CW low Cd         C-2         30         15         56         370         22         10         220         220           For Worker Autra with Low Cd         22         14         72         146         170         220         170         170           FO Weater         C-1         29         6.1         24         700         22         14         340         430           FO Weater         C-3         28         6.1         24         700         22         16         630         472           FO Weater Autra with Low Cd         28         6.1         24         700         22         16         455         451           FO Night Cd         C-1         60         19         43         760         22         16         455         170           CW Night Cd         C-1         60         17         24         400         22         16         455         170           CW Night Cd         C-1         60         17         26         22         16         450         170	90	CW low Cd	3	:	5	78	8	22	=	ı	ı	1	1
CW low Cd   C-2   30   15   56   370   22   10   230	90	CW low Cd	2	8	2	2	96	22	9	9	170	910	902
Flow Mater Runs with Low Cd   22   14   72   361   1.8   13   146   178   17	70.7	CW low Cd	3	8	5	8	370	22	2	82	230	\$	280
RO Water         C-1         29         6.1         24         530         22         14         340         430           RO Water         C-2         29         6.1         24         700         22         19         630         472           RO Water         C-3         29         6.1         24         700         22         19         452           RO Motor Router Runs with Low Cd         28         6.1         24         643         22         16         451           RO (D.O.)         C-1         60         19         43         760         22         16         451         170           CW high Cd         C-1         60         17         26         430         22         12         420         170           CW high Cd         C-1         60         17         26         430         22         12         330         270           CW high Cd         C-2         62         16         26         560         22         15         820         370           EM high Cd         C-2         63         16         26         560         22         15         820         370	tverage for (	City Water Aura	ath Low Cd	8	=	22	361	1.0	t)	140	178	358	204
NO Waler   C-2   25   6.1   24   700   22   19   630   472   640   630   472   640   630	9	RO Water	រ	8	5.0	72	830	22	=	340	430	1140	270
FO Weller   C-3   29   6.1   24   700   22   19         FO (D.O.)   C-1   60   19   43   760   22   19   465   451     FO (D.O.)   C-1   60   17   26   430   22   12   330   270     CW high Cd   C-2   60   19   26   550   22   15   520   330     CW high Cd   C-2   60   16   27   460   22   13   425   330     CW high Cd   C-2   60   16   27   460   22   13   425   330	90	RO Water	3	8		72	92	22	2	93	472	1600	280
For Motive Rurs with Law Cd   26   6.1   24   643   2.2   16   465   451   451   450   170   1	01-24	RO Webs	3	8		55	200	22	2	ı	1	ı	280
FO (D.O.)   C-1   80   19   43   760   22   21   420   170	Iverage for I	AO Weter Avre a	et Low Cd	8	6.1	72	8	22	=	465	451	1370	283
CW high Cd         C-1         66         17         26         430         22         12         330         270           CW high Cd         C-2         83         16         26         850         22         15         620         330           In Start Cally Wistor Rura with High Cd         76         16         27         490         22         13         425         300	11-26	RO (0.0.)	2	8	2	43	760	2.2	2	92	5	780	170
CW Night Cd   C-2   850   19   26   850   2.2   15   620   330   19   640   10   2.2   13   425   300	JC-12	CW Ngh Cd	2	8	12	28	430	22	12	330	270	8	52
for City Wheer Runs with High Cd 76 18 27 490 22 19 425 300	3C-13	CW Ngh Cd	3	8	2	8	88	2.2	5	22	88	98	110
	Average for	City Week Rute	with High Cd	۶	=	27	8	. 22	C.	\$3	300	305	115

Source: Arthur D. Little, Inc.

- Cd<sup>2+</sup> resin capacity increases as the non-Cd<sup>2+</sup> cation concentration of the solution decreases (at constant non-Cd<sup>2+</sup> cation: Cd<sup>2+</sup> molar ratio); and
- Cd2+ resin capacity increases as the non-Cd2+ cation:Cd2+ molar ratio decreases.

A model was developed using laboratory data to predict Cd<sup>2+</sup> resin capacities from the Cd<sup>2+</sup> concentration and concentration of competing cation species (primarily Na<sup>+</sup>). The highest capacities are achieved at high Cd2+ concentration and low non-Cd2+ cation species concentration. These relationships can be seen by the correlation between the observed and predicted Cd2+ resin capacities for each run as shown in Figure 5-1. The model closely predicted resin capacities except Run BC-11 (treatment of the water discharged from the ERU) where the observed Cd2+ resin capacity was 420 meg/L and the predicted capacity was approximately 170 meg/L. Runs BC-9 and BC-13 also had an actual Cd2+ resin capacity that was higher than the predicted value; however, the reason for this difference is that the lead column in these two runs was initially loaded as a polishing column, and the cation concentration from the lead column to the polishing column is less than the cation concentration of feed solution which was used to predict the actual Cd<sup>2+</sup> resin capacity. Use of the cation concentration from the lead column to develop the predicted value would have correlated better, but this value was not available. Figure 5-2 shows the actual and predicted values for cation resin capacities for each type of rinsewater treated. As demonstrated by the results shown in Figure 5-2, minimizing the competing cation concentrations through the use of RO treated rinsewater will provide the highest Cd<sup>2+</sup> resin capacity.

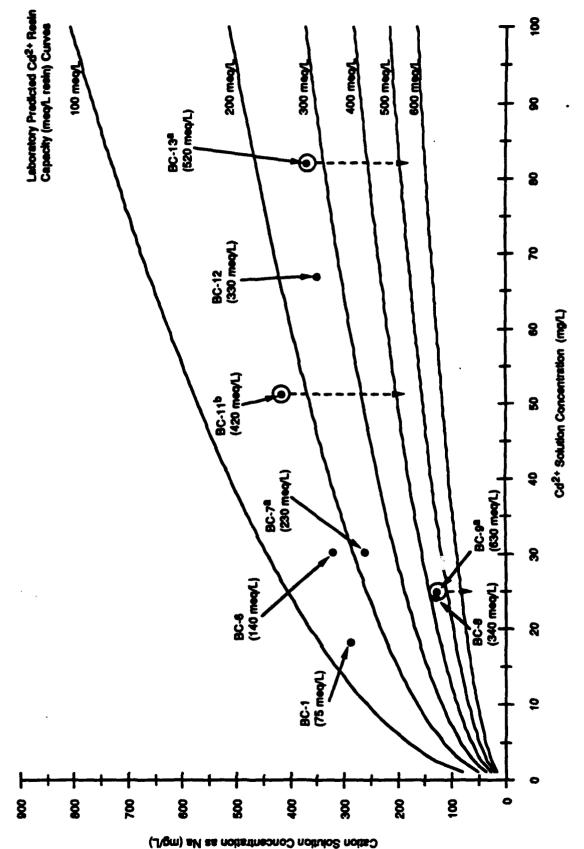
As a result of the close correlation, the use of the Na-Cd equilibrium constant calculated in the laboratory tests is a valid method for developing full-scale design parameters for treatment of the rinsewaters from the Cd<sup>2+</sup> plating operations.

Specifically for North Island's plating operations, the ability to treat four types of plating rinsewaters was investigated to determine what the actual Cd<sup>2+</sup> resin capacity for that wastewater would be and to evaluate the ability of the treatment system to meet regulatory discharge criteria. The results for the Cd<sup>2+</sup> resin capacity are presented below and the ability to meet regulatory discharge criteria are presented in Section 5.2.1.2, Compliance with Regulatory Limits.

City Water with Low Cadmium Concentration. The first seven pilot test runs (Runs BC-1 through BC-7) were based on analyses of the North Island Cd-CN plating rinsewater tank taken during the design of the pilot plant which indicated a Cd<sup>2+</sup> concentration of approximately 22 mg/L. To generate process rinsewater with this concentration, a North Island plating solution was diluted 1:1000 to obtain an average: Cd<sup>2+</sup> concentration of 22 mg/L; CN- concentration of approximately 58 mg/L; and cation concentration of 14 meq/L (cation:Cd molar ratio of 72). The results of the pilot test runs showed an average Cd<sup>2+</sup> resin capacity of 150 meq/L and an average complete breakthrough volume of 360 bed volumes (BV).

Source: Arthur D. Little, Inc.

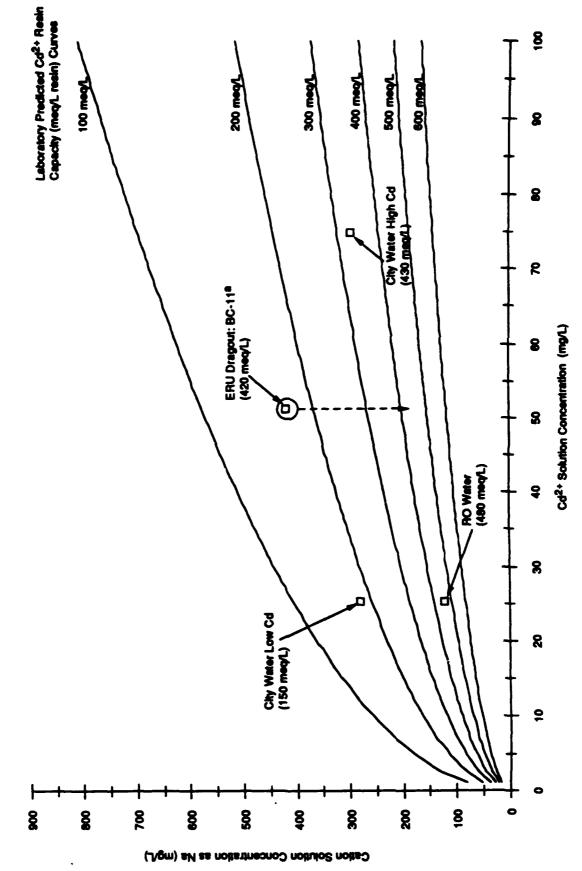
Figure 5-1: Observed Cd2+ Resin Capacities for Each Run Plotted on Cd-Cation Equilibrium Curves



a These runs were performed with the resin initially being loaded as the polithing column. The dotted fine shows the difference between predicted and

<sup>b</sup> This run was the ERU dragout run. The reason for the difference between the solutel and predicted Cd capacities is unknown. The dotted line shows the difference between predicted and actual.

Figure 5-2: Average Cd<sup>2+</sup> Resin Capacities for Each Type of Rinse Water Plotted on Cd-Cation Equilibrium Curves



<sup>®</sup> This run was the ERU dragout run. The reason for the difference between the actual and predicted Cd capacities is unknown. The dotted line shows the difference between predicted and actual.

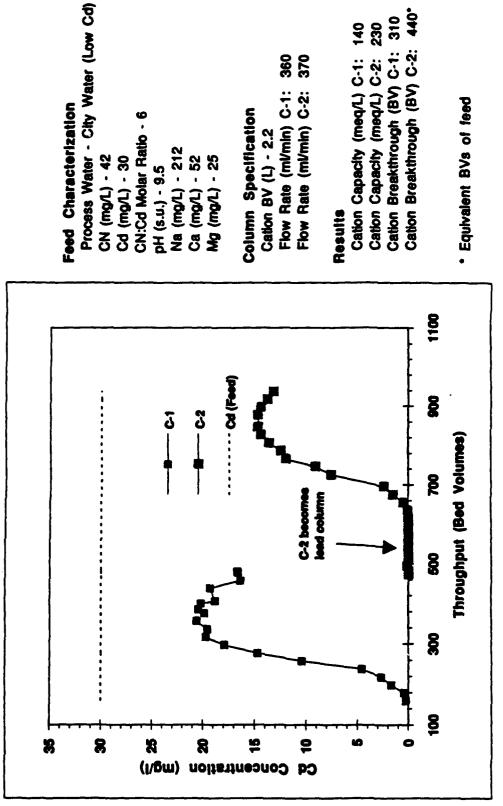
Figure 5-3 presents the Cd<sup>2+</sup> breakthrough curves for Runs BC-6 and BC-7. The Cd<sup>2+</sup> breakthrough curves for both runs leveled off prior to reaching the feed concentration of Cd<sup>2+</sup>. This leveling off occurred in all the city water runs that reached complete breakthrough; this phenomenom is discussed further in Section 5.2.1.3, Operational Difficulties. The breakthrough curves for Runs BC-6 and BC-7 also demonstrate that the polishing column has a higher Cd<sup>2+</sup> resin capacity and complete breakthrough volume than the lead column. The reason for this difference is caused by the fact that the polishing column is initially loaded from the effluent of the lead column. The lead column removes some of the cations and limits the cation concentration that the polishing column must treat; thereby increasing the polishing column's Cd<sup>2+</sup> resin capacity and complete breakthrough volume, by lowering the cation: Cd molar ratio.

City Water with High Cadmium Concentration (actual rinsewater). During the pilot test program, the plating rinsewater handling procedures were changed at the North Island facility to eliminate discharges from the Cd<sup>2+</sup> rinse tank to the IWTP. Because the plating rinsewater could no longer be discharged to the IWTP, the volume of rinsewater generated by the facility was reduced by holding the water in the plating rinse tank for longer periods of time. This resulted in an average Cd<sup>2+</sup> concentration of 76 mg/L, average CN- concentration of 77 mg/L, and average cation concentration of 18 meq/L (cation:Cd molar ratio of 30). To determine the ability of the ion exchange system to treat the current actual conditions in the plating shop, runs BC-12 and BC-13 were conducted with plating rinsewater taken directly from the rinse tank. The results of the pilot plant runs showed an average Cd<sup>2+</sup> resin capacity of 430 meq/L and an average complete-breakthrough volume of 390 BV. The Cd<sup>2+</sup> resin capacity for this set of runs was higher than for the other runs with city water due to the lower cation:Cd molar ratio in this set of runs.

Figure 5-4 presents the Cd<sup>2+</sup> breakthrough curves for runs BC-12 and BC-13. These breakthrough curves had similar features to the other city water runs but they also showed leakage of Cd<sup>2+</sup> when the columns were put on-line. The leakage is believed to have been caused by the high regeneration flow rate (2.7 BV/hr) and is discussed in detail in Section 5.2.1.2, Compliance with Regulatory Criteria and in Section 5.3.1, Cation Regeneration.

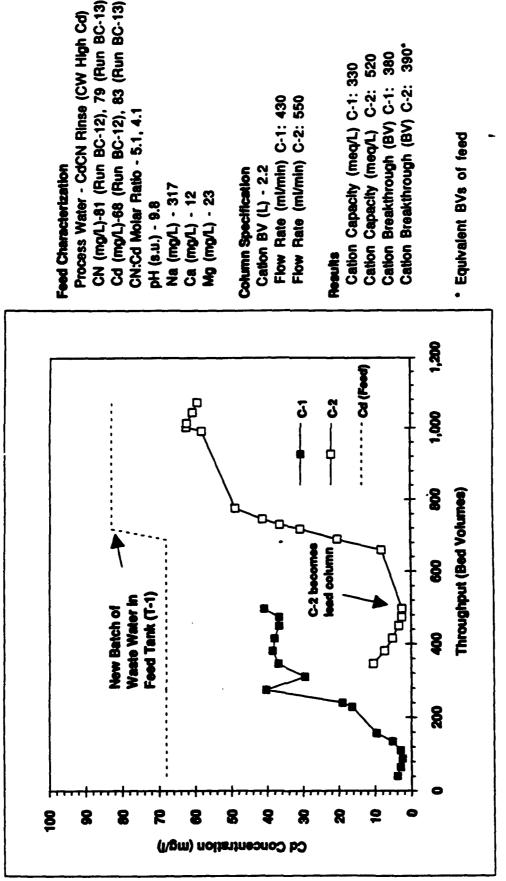
RO Water. Because of the high cation concentration of the city water and the resulting low Cd<sup>2+</sup> resin capacities, Runs BC-8 through BC-10 were conducted utilizing RO water to dilute the plating solution. The resultant rinsewater had the following average composition: Cd<sup>2+</sup> concentration of approximately 24 mg/L; CN- concentration of approximately 55 mg/L; and cation concentration of 6 meq/L (cation:Cd molar ratio of 25). The RO water was generated at North Island by taking city water and processing it through an RO unit to remove a significant amount of the anion and cation species. The RO treatment of the city water reduced the overall cation concentration by about one-half. The results of the pilot testing with RO water showed an average Cd<sup>2+</sup> resin capacity of 480 meq/L and an average complete-breakthrough volume of 1400 BV. The

Figure 5-3: Columns C-1 and C-2 Breakthroughs (Runs BC-6 and BC-7) 6/8-6/11



Source: Arthur D. Little, Inc.

Equivalent BVs of feed



Source: Arthur D. Little, Inc.

• Equivalent BVs of feed

380 520

Cd<sup>2+</sup> resin capacity for this set of runs was higher than for the runs with city water and a low Cd<sup>2+</sup> concentration, due to the lower cation:Cd molar ratio in this set of runs. With higher Cd<sup>2+</sup> concentration, the Cd<sup>2+</sup> resin capacity of the RO water runs was almost identical to that of the city water runs because of the similar cation:Cd molar ratio.

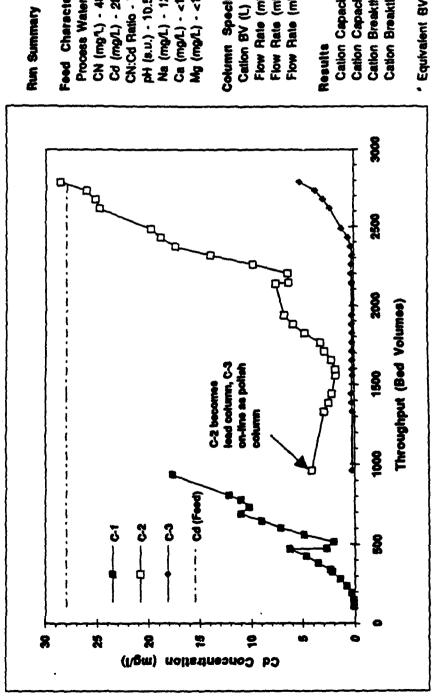
Figure 5-5 (Runs RC-8, RC-9, and RC-10) shows breakthrough curves for three runs conducted in series, utilizing RO water to make up the plating rinsewater batch. The complete-breakthrough volume was considerably larger than for the city water runs as predicted by the laboratory model, due to the lower concentrations of competing cations present in the water. In addition, the breakthrough reached the feed concentration for Run BC-9, and Run BC-8 appears as though it would have also reached the feed concentration. It should also be noted that Run BC-9 had Cd<sup>2+</sup> leakage when it was put on-line. Like the other runs where Cd<sup>2+</sup> leakage is believed to have been observed, the leakage was caused by the high sulfuric acid regeneration flow rate and is discussed in detail in Section 5.2.1.2, Compliance with Regulatory Limits and in Section 5.3.1, Cation Regeneration.

Electrolytically Treated Dragout Water. An additional set of test runs was conducted to evaluate the ion exchange treatment of the discharge from an electrolytic recovery unit (ERU). Plating solution was diluted with RO water to approximately 1000 mg/L Cd<sup>2+</sup> and 1800 mg/L CN<sup>-</sup>. The diluted plating solution was then processed through an electrolytic recovery unit until the Cd<sup>2+</sup> concentration was reduced to approximately 350 mg/L (Figure 5-6). The solution was then diluted with RO water in the feed tank for processing through the ion exchange system (Run BC-11). The characterization of the water showed an average Cd<sup>2+</sup> concentration of approximately 50 mg/L, an average CN- concentration of approximately 180 mg/L, and an average cation concentration of 20 meg/L (cation:Cd molar ratio of 43). The results of the pilot plant showed a Cd<sup>2+</sup> resin capacity of 420 meg/L and a complete-breakthrough volume of 750 BV. The Cd<sup>2+</sup> resin capacity for this set of runs was similar to that of the RO water runs and to that of the city water runs with the high Cd2+ concentration; however, the laboratory model predicted a lower Cd<sup>2+</sup> resin capacity than actually observed. The reason for the difference between the observed and predicted values is unknown. Figure 5-7 presents the Cd<sup>2+</sup> breakthrough curve for the electrolytically treated dragout water run.

**5.2.1.2 Compliance with Regulatory Limits.** In determining if the cation exchange system would be able to comply with regulatory limits, two discharges from the columns were monitored:

- Leakage of Cd<sup>2+</sup> from a newly regenerated column; and
- Regulatory breakthrough of the polishing column.

Figure 5-5: Columns C-1, C-2, and C-3 Breakthroughs (Runs BC-8, BC-9, and BC-10) 6/15-6/23



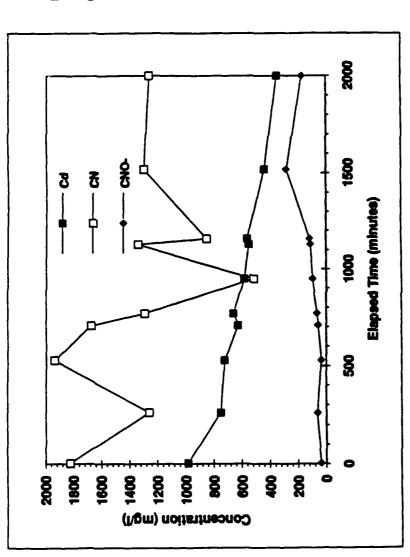
Process Water - RO Water Feed Characterization Column Specification Cation BV (L) - 2.2 Na (mg/L) - 125 Ca (mg/L) - <1 CN:Cd Ratio - 7.4 CN (mg/L) - 48 Cd (mg/L) - 28 pH (s.u.) - 10.5 Mg (mg/L) - <1

630 Cation Capacity (meq/L) C-1: 340 8 8 8 Flow Rate (ml/min) C-3: Flow Rate (ml/min) C-1: Flow Rate (ml/min) C-2:

1600 1140 Cation Capacity (meq.L.) C-2: 6 Cation Breakthrough (BV) C-1: Cation Breakthrough (BV) C-2:

\* Equivalent BVs of feed

Figure 5-6: Dragout Simulation ERU Run



# Run Summary

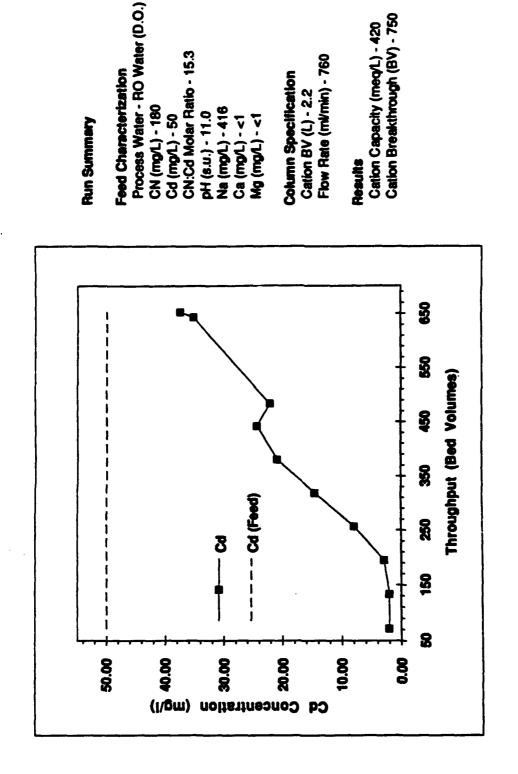
# Characterization Initial Cd concentration (mg/L) - 1000 Initial CN Concentration (mg/L) - 1800 Initial CNO- Concentration (mg/L) - 36 Volume (L) - 227 Current density = 0.3-0.4 Asf

# Results

Final Cd Concentration (mg/L) - 351 Final CN Concentration (mg/L) - 1260 Final CNO- Concentration (mg/L) - 200

Recovered 147 g Cd = 65%

Figure 5-7: Column C-1 Breakthrough (Run BC-11) 6/24-6/25



The Federal Pretreatment Standards for Metal Finishers (Existing Sources) mandates a cadmium compliance limit of 0.69 mg/L for a daily maximum and a 0.26 mg/L for an average monthly concentration for total cadmium in the effluent from metal finishing operations 10. The effluent from the cation polishing columns during pilot testing was below this level for seven runs. However, cadmium leakage was observed in excess of the daily maximum at the beginning of six runs. In the runs where Cd<sup>2+</sup> leakage was observed, two types of exceedances were noted:

- 1) The first sample taken from the column had a Cd2+ concentration above the daily limit, but the samples thereafter had Cd2+ concentrations below the limit; and
- 2) The first sample taken from the column had a Cd<sup>2+</sup> concentration above the daily limit, and the concentration slowly declined over the next several samples.

The first type of leakage was probably a result of a deadleg in the piping of the pilot system where water containing a high concentration of Cd<sup>2+</sup> from the previous run or the regeneration was retained and ultimately contaminated the first sample. The second type of leakage occurred when the column was regenerated at a flow rate greater than 2.2 BV/hour. The leakage of Cd<sup>2+</sup> at the higher regeneration flow rate was probably caused by inefficient regeneration of the cation resin which left low levels of Cd<sup>2+</sup> on the resin to slowly leak off when it was put back on-line. The slow leakage of contaminants did not occur when a slower regeneration flow rate was used; therefore, a flow rate slower than 2.2 BV/hr has been recommended for the full-scale design. In addition to operating the regeneration at a lower flow rate, the full-scale design requires that the first 10 bed volumes of effluent from a new column be recycled back to the feed tank to ensure that the regulatory limits will not temporarily be exceeded due to contaminated water retained in the column.

Review of the Cd<sup>2+</sup> resin capacities and the regulatory breakthrough of Cd<sup>2+</sup> in the polishing column (the point where the cadmium concentration in the effluent of the polishing column exceeds the regulatory discharge limit) for both the city water and the RO water provided the necessary information to determine how each cation system would have to be operated for each type of plating rinsewater in order to comply with regulatory limits. Control of the cation system when processing city water can be accomplished by monitoring the effluent from the lead column for Cd<sup>2+</sup>. The effluent from the polishing column remains in compliance even when the lead column has reached full breakthrough. Therefore, complete breakthrough of the lead column indicates when the lead column should be taken off-line to be regenerated and the polishing column should be moved to the lead column position. A fresh polishing column would then be put on-line to ensure compliance. This type of control is desirable in that it provides a sufficient backup to ensure that the regulatory limit in the effluent discharge is continuously met in the event the lead column has broken through and the analytical results of the lead column effluent samples have been delayed.

Therefore, the three column arrangement (two columns on-line while one is being regenerated) is satisfactory when processing the city water.

While the volume of RO rinsewater which can be treated before the regulatory limit is exceeded is greater than with city water, the effluent from the polishing column exceeds the compliance limit before the lead column reaches full breakthrough. Thus, the Cd<sup>2+</sup> concentration in the effluent from the polishing column becomes the control point when two columns in series are used. This does not provide a backup in the event the effluent Cd<sup>2+</sup> concentration begins to rise above the compliance limit while the effluent sample is being analyzed. If the treated rinsewater is recycled, this slight rise in Cd<sup>2+</sup> concentration will not cause a violation, however, the system will require careful monitoring. One way to ensure compliance is to utilize a four column arrangement with one lead column and two polishing columns, and one off-line being regenerated. The control point becomes the effluent from the first polishing column. When the first polishing column reaches the regulatory breakthrough, the lead column is taken off-line (for regeneration) and a fresh final polishing column is put on-line. This results in a more complicated piping system and an increase in the capital and operating costs of approximately 20%.

# 5.2.1.3 Operational Difficulties.

On-Site Breakthrough Monitoring of Cadmium. Three different analytical methods were used for measuring Cd<sup>2+</sup> in the effluent of the cation columns during the pilot program, including:

- The use of a cadmium-specific ion electrode;
- Free CN-correlation with Cd-CN complex using the cyanide Hach® kit; and
- Analysis for Cd<sup>2+</sup> using the cadmium Hach® kit.

The cadmium-specific ion electrode did not provide any measurement of the Cd<sup>2+</sup> concentration in the effluent because it could not detect the Cd<sup>2+</sup> that was complexed with CN<sup>-</sup>. The second method involved the measurement of the free CN<sup>-</sup> concentration from the cation column effluent. This method is based on the dissociation of the Cd<sup>-</sup>CN complex by the resin. The free CN<sup>-</sup> concentration in the effluent will be higher when Cd<sup>2+</sup> is not present, but will decrease as Cd<sup>2+</sup> concentration increases in the effluent, due to binding of free CN<sup>-</sup> with Cd<sup>2+</sup>. This method was not sensitive enough to determine the change in free CN<sup>-</sup> concentration as breakthrough began and therefore gave an inaccurate indication of Cd<sup>2+</sup> breakthrough.

The third method was the most successful, and involved the use of a cadmium test kit by Hach® which utilized chemical reagents that react with the Cd<sup>2+</sup> causing a color change which could be measured by a colorimeter. The method was successful, but not completely reliable. Some errors were encountered due to the sensitivity of the test

method which ranged from 1 to  $70 \,\mu g/L$ , and thus required large and accurate dilutions for each sample. The high sensitivity of the test procedure required that all glassware used for the test be washed with an acid solution to prevent cross-contamination from previous samples. The combination of high sensitivity, acid cleaning requirements, and the available facilities at the pilot plant for cleaning glassware promoted errors and thus did not always provide an accurate indication of breakthrough. In addition to the sensitivity of the test, the method required the use of several chemical reagents which are considered hazardous, including: chloroform, cyanide, and dithizone. These hazardous reagents require careful handling and proper disposal.

Because of the difficulties monitoring for Cd<sup>2+</sup> in the effluent from the cation columns, some runs were inadvertently stopped before complete breakthrough; however, a greater concern is the selection of an analytical method for use in a full-scale system to ensure that the ion exchange treatment system effluent is in compliance with discharge regulations. Based on the results of the pilot tests, the cadmium test kit Hach® is the best method for on-site analysis although a hood and adequate analytical glassware would have to be supplied if the method were used to monitor a full-scale system. The recommended method for monitoring, however, would be an arrangement with an analytical laboratory on the base or with a laboratory close by to perform the effluent analyses quickly (24-hour turnaround) utilizing either atomic absorption (AA) or an inductively coupled plasma (ICP) spectrometer (as was used to develop the breakthrough curves for this pilot test program).

Flow to the Ion Exchange System. During the operation of the pilot system, the flow rate from the feed tank to the ion exchange system fluctuated due to (1) buildup of suspended solids in the feed filter, (2) varying pressure drops depending upon the column configuration, and (3) varying levels of water in the feed tank (T-1). Constant attention and adjustment was required to maintain a constant flow rate, and when the system was left unattended during the night, the flow rate often decreased significantly. To account for the variation in the flow rate, the rate was set higher at night to compensate for the anticipated gradual decrease.

The fluctuation in the flow rate made it difficult to control the actual flow rate during any given run. Therefore, an average flow rate was calculated for each column by dividing the quantity of wastewater processed through the column by the length of time the column was on-line. It is important to note, however, that columns that were on-line together during a portion of a run may have different average flow rates since each column was not on-line for the same length of time and processed different amounts of water.

An additional concern, related to the flow rate to the ion exchange system, is the amount of suspended solids in the feed and the number of filter cartridges that would be needed during continuous operation. During the runs with city water, the filters were

changed every 125 to 250 gallons of throughput or when the upstream pressure reached 5 to 6 psig. The RO water runs used significantly fewer filters because the concentration of solids in the water was lower. During these runs, the filters were changed every 800 gallons throughput or when the upstream pressure reached 5 to 6 psig.

Leveling Off of Cadmium Breakthrough. During the runs which utilized city water, the concentration of Cd<sup>2+</sup> in the effluent of the lead column steadily rose until it leveled off. The concentration at which Cd<sup>2+</sup> leveled off, however, was approximately 33% lower than the feed concentration. This is shown in Figure 5-3 which illustrates columns C-1 and C-2 operating in series (Runs BC-6 and BC-7). The leveling off of the Cd<sup>2+</sup> breakthrough was found to be a common occurrence for all runs utilizing city water including runs BC-12 and BC-13 which utilized actual plating rinsewater. The concentration leveled off at 20 to 30 mg/L below the feed concentration for BC-12 and BC-13 which was approximately 33% lower than the feed concentration. Figure 5-4 illustrates runs BC-12 and BC-13 (columns C-1 and C-2 in series).

To determine whether or not there was a cadmium precipitate being removed in the process filter ahead of the process pump which would account for the low breakthrough concentrations, both total and dissolved Cd<sup>2+</sup> were analyzed for in the feed tank T-1 during the city water runs. Table 5-3 shows that the dissolved and total Cd<sup>2+</sup> concentrations are identical and therefore, the filter could not have caused the low breakthrough concentrations. The conclusion can be drawn that the ion exchange columns removed the portion of Cd<sup>2+</sup> after the effluent concentration had leveled off.

The removal of this portion of the Cd<sup>2+</sup> by the columns is further supported by the Cd<sup>2+</sup> recovery data developed from the regeneration curves and discussed in Section 5.3.1 of this report. When only the Cd<sup>2+</sup> loading based on the breakthrough concentration was taken into account, the percent recovery from regeneration was much greater than 100%. However, when the entire Cd<sup>2+</sup> loading (based on the feed concentration) was taken into account, the recoveries approached 100%.

The cause of the lower Cd<sup>2+</sup> concentrations in the effluent stream at breakthrough is unknown; however, the cause could be either an interference with the analytical method or a removal mechanism other than on the ion exchange resin active sites. It is postulated that the Cd<sup>2+</sup> may be reacting with the residual NaOH left in the column from the regeneration phase, forming an insoluble species such as cadmium hydroxide [Cd(OH<sub>2</sub>)] or cadmium carbonate (CdCO<sub>3</sub>). This cannot be substantiated, however, since the same phenomenon is not exhibited in the RO water runs where the pH and CO<sub>3</sub><sup>2-</sup> is even higher.

#### 5.2.2 Anion Column Results

Table 5-5 summarized the seven anion exchange runs conducted during the seven-week pilot plant operation. The objectives of conducting numerous runs at varying conditions were as follows:

- Evaluate CN- resin capacity at different CN- and anion concentrations;
- Evaluate the ability of the laboratory model to accurately predict CN- resin capacity;
- Evaluate the potential for CN-recovery and reuse;
- Evaluate the use of ion exchange for CN- removal and recovery from dragout solutions processed in an electrolytic recovery unit;
- Evaluate compliance with regulatory limits; and
- Identify both actual and potential operational problems.

5.2.2.1 Cyanide Resin Capacity. Because of the high concentration of other anions in the rinsewater, the OH-CN- resin capacity model developed in the laboratory study was not valid and could not be used to predict the actual CN- breakthrough. While the model was not able to predict the actual CN- resin capacity, the results did show that as the cyanide concentration decreased, the resin capacity decreased, as demonstrated in the laboratory study.

The pilot test also demonstrated that the high concentration of other anions coupled with a low affinity of the anion resin for CN- produced a breakthrough curve where CN-quickly broke through the resin bed at the regulatory limit and then slowly reached the complete breakthrough. The swift breakthrough caused the polishing column to also reach the regulatory breakthrough rapidly, usually within 20 to 30 bed volumes; therefore, the anion columns were quickly out of compliance with the Federal Pretreatment Standards for Metal Finishers (compliance limit of 1.2 mg/L Total Cyanide [TCN] daily maximum and 0.65 mg/L average monthly<sup>10</sup>). The effluent from the polishing column was unable to maintain this compliance level for more than a few hours after being put on-line. In order to maintain compliance for even a complete day the volume of anion resin would have to be increased by a factor of at least 10.

City Water with a low CN- Concentration. The first three pilot plant runs were based on analyses of the North Island Cd-CN plating rinsewater tank taken during the design of the pilot plant which indicated a CN- concentration of approximately 58 mg/L. To generate process rinsewater with this concentration, plating solution was diluted 1:1000 with city water to obtain an average CN- concentration of 58 mg/L, an average

Table 5-5: Summary Anion Column Capacity

Property   Property   Land   City   Anderson   Paris   Anderson   Paris   Anderson   Companies   Com					•	Sea Chemeter	teston			cification		Ann Calum Re	1
	,]	]]	3]	8 ]	ļį	1 3	Antonicki Mater State	1 1	Wilder and				
City Wester   A-1   58   14   62   6   300   2.5   7   160   170     City Wester   A-3   58   14   6.2   6   300   2.5   7   160   170     NO Vision   A-1   40   7.8   10.7   4   770   2.5   14   120   170     NO (No.0.)   A-1   40   7.8   10.7   4   670   2.5   16   160   160     NO (D.O.)   A-1   40   27   11   4   670   2.5   16   466   105     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   160   27   11   4   1060   2.5   21   446   143     NO (D.O.)   A-2   A-3   A-4   A-4   A-4   A-4   A-4   A-4   A-4     NO (D.O.)   A-3   A-4   A-4   A-4   A-4   A-4   A-4   A-4     NO (D.O.)   A-3   A-4   A-4   A-4   A-4   A-4   A-4   A-4     NO (D.O.)   A-4   A-4   A-4   A-4   A-4   A-4   A-4   A-4     NO (D.O.)   A-4   A-4   A-4   A-4   A-4   A-4   A-4   A-4     NO (D.O.)   A-4   A-4   A-4   A-4   A-4   A-4   A-4   A-4     NO (D.O.)   A-4   A-4   A-4   A-4   A-4   A-4   A-4   A-4   A-4     NO (D.O.)   A-4     NO (D.O.)   A-4   A-4   A-4   A-4   A-4   A-4   A-4   A-4   A-4     NO (D.O.)   A-4     NO (D.O.)   A-4   A-4   A-4   A-4   A-4	3	Cay Weder	14	8	=	0.2	•	902	2.5	8	1	-	1
City Wester   A-3   St	M-2	City Weeker	₩.	8	2	0.5	•	8	2.5	^	8	•	12 (4)
NO Window   A-1   A-1	-	Chymen.	3	8	ī	6.2	•	8	2.5	~	3	٤	3.
NO Wester   A-1   47   8.1   10.6   4   600   2.5   14   120   170   170   180   1	herage for 5	WWA.	# (m C)	8	=	82	•	287	2.5	9	381	129	12
NO Week   A-1   A-1   A-2   10.7   4   750   2.5   10   20	}	NO Week	4	5		10.6	•	8	2.5	*	120	170	15 (a)
RO (D.O.)         A-1         180         27         11         4         675         2.5         16         100         165           RO (D.O.)         A-2         180         27         11         4         670         2.5         16         465         105           RO (D.O.)         A-2         180         27         11         4         1060         2.5         25         410         160           RO (D.O.)         A-2         180         27         11         4         865         2.5         21         448         143	-	NO Week	₹	*	7.0	10.7	•	750	5.5	:	98	<b>302</b>	(E)
MO (0.0.)   A-1   190   27   11   4   670   2.5   16   485   105   106   100   2.5   25   410   100	horage for /		4	8	0.0	10.7	•	678	2.5	2	961	196	2
MO (0.0.)   A.2   180   27   11   4   1080   2.5   25   410   180   180   180   180   180   183   18	3	RO (0.0.)	¥	\$	22	=	•	670	2.5		\$	105	9 (4)
180 27 11 4 865 2.5 21 448 143	K-7	NO (0:0:)	**	<u>§</u>	27	=	•	2080	2.5	8	9	8	3
	harape for L	Pochobytosty Tre	need RO Water	8	27	=	•	3	2.5	12	3	143	8

(a) Regulatory first was exceeded in the first eartpile.

Cd<sup>2+</sup> concentration of approximately 22 mg/L, and an average anion concentration of 14 meq/L. The average CN- resin capacity for the city water runs was approximately 140 meq/L and had a complete-breakthrough volume of 130 BV; however, in the runs where a breakthrough curve was developed, the first sample from the column exceeded the daily regulatory limits (CN- concentration of 1.2 mg/L). This quick regulatory breakthrough (an average of 12 BV) significantly limits the ability to use the anion exchange system to treat the plating rinsewater and comply with the regulatory limit. Figure 5-8 presents the breakthrough curve for Run BA-3.

RO Water. Because of the high anion concentration of the city water and the resulting low CN- resin capacities, runs BA-4 and BA-5 were conducted utilizing RO water to dilute the plating solution to an average CN- concentration of approximately 48 mg/L, an average Cd<sup>2+</sup> concentration of approximately 28 mg/L, and an average anion concentration of 6 meq/L. The RO water was generated at North Island by taking city water and processing it through an RO unit to remove a significant amounts of the anion and cation species. The treatment of the city water halved the anion concentration. The results of the pilot plant runs with RO water showed an average CN-resin capacity of 190 meq/L and an average complete-breakthrough volume of 190 BV. The CN- resin capacity for this set of runs was higher than for the runs with city water and a low CN-concentration due to the lower anion concentration in this set of runs. However, even with the lower anion concentration, the first sample from the column exceeded the regulatory limit (CN-concentration of 1.2 mg/L).

Figure 5-9 presents a breakthrough curve for Run BA-4 using RO water. The gradual reduction in CN-concentration in the feed is attributed to CN-oxidation and degradation throughout the system. This is further supported by the data collected from T-1 which show that the initial CN-concentration is always the highest and that day by day it steadily declines. The concentration of CNO-was also monitored in T-1 and was found to increase from 1 mg/L to 2-3 mg/L. Because of the low concentration of CNO-in the feed, it does not appear that CNO-significantly affects the anion resin loading.

The other RO water run, BA-5, exhibited a two-step breakthrough curve. The second step, however, occurred after the system was required to shut down for the weekend. The jump in cyanide concentration after the weekend shutdown could be due to the cyanide reaching equilibrium with the solution in the column and exchanging for the other ions in solution.

Electrolytically Treated Dragout Water. An additional set of runs was conducted to evaluate the ion exchange treatment of the discharge from an electrolytic recovery unit (ERU). Plating solution was diluted with RO water to approximately 1000 mg/L Cd<sup>2+</sup> and 1800 mg/L CN<sup>-</sup>. The diluted plating solution was then processed through an ERU until the Cd<sup>2+</sup> concentration was reduced to approximately 350 mg/L (Figure 5-6). The solution was then diluted with RO water in the feed tank for processing through the ion

Figure 5-8: Column A-3 Breakthrough (Run BA-3) 4/14-4/15

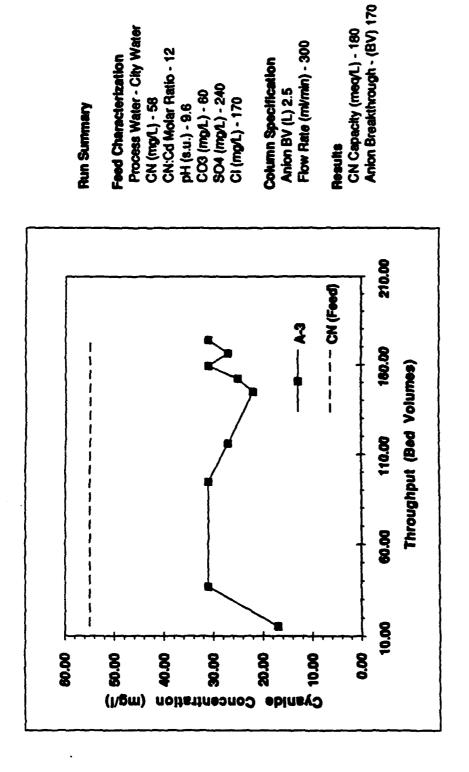
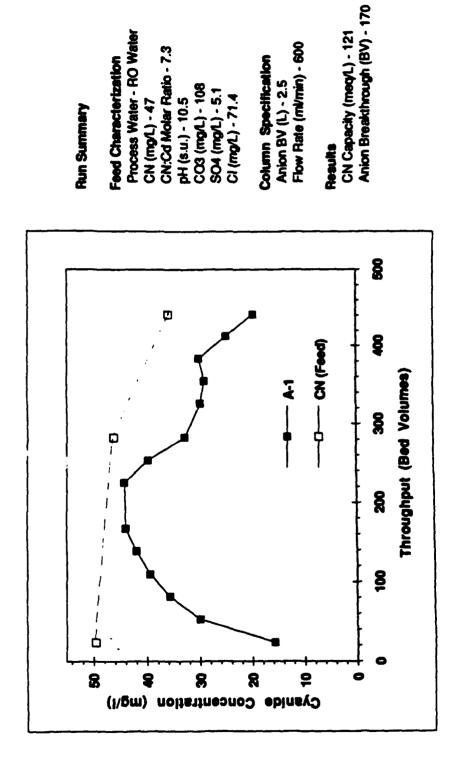


Figure 5-9: Column A-1 Breakthrough (Run BA-4) 6/15-6/16

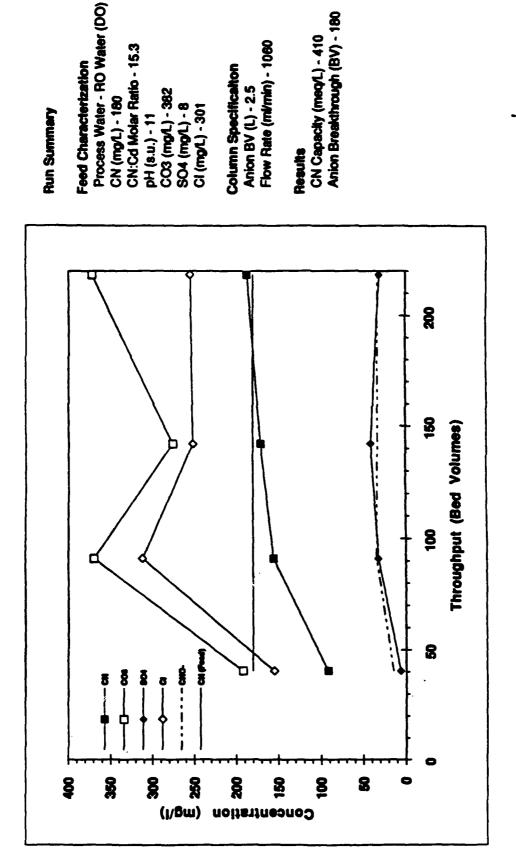


exchange system (Runs BA-6 and BA-7). The characterization of the water showed an average CN- concentration of approximately 180 mg/L, an average Cd<sup>2+</sup> concentration of approximately 50 mg/L, and an average anion concentration of 27 meq/L. The results of the pilot plant showed a CN- resin capacity of 450 meq/L and an average complete-breakthrough volume of 140 BV. The results of these runs demonstrated a significantly better CN- resin capacity than was observed in either the city water or RO water runs. The reason for this is the large increase in the CN- concentration in the feed stream. (In addition, the capacity increase could have been affected by the Cd-CN complex in the effluent of the cation column which has a higher affinity for the anion resin than does free CN-. Some Cd-CN leakage did occur during these runs because no cation polish column was on-line.) However, even with the higher CN- resin capacities, the CN- concentration in the effluent reached the regulatory limit within the first few bed volumes.

As shown in Figure 5-10, not only is  $CN^-$  breaking through the column, but also sulfate  $(SO_4^{2-})$ , cyanate  $(CNO^-)$ , carbonate  $(CO_3^{2-})$ , and chloride  $(Cl^-)$  ions. The concentrations of these species gradually rises and then breaks through, indicating that all are being removed by the resin.

- 5.2.2.2 Compliance with Regulatory Limits. The Federal Pretreatment Standards for Metal Finishers for Existing Facilities indicate a total cyanide daily maximum of 1.2 mg/L for cyanide and an monthly average of 0.65 mg/L. This discharge limit would be difficult to maintain with the ion exchange system since CN-concentration reached the regulatory limit in the effluent in the first few bed volumes. Compliance with the daily maximum limit was only observed in the effluent of the polishing column for approximately eight hours (30 bed volumes) at a flow rate of 300 ml/min in the effluent from the polishing column, after which the concentration rose above the compliance limit.
- 5.2.2.3 Monitoring Cyanide Breakthrough. For monitoring the CN- breakthrough of the anion columns, both a cyanide Hach® test kit and a cyanide-specific ion electrode were used. Both test methods were adequate but required accurate dilutions to bring the solution concentrations within the operating range of the test method. The Hach® kit worked well, but each sample required 30 minutes to fully develop its color before examination in the colorimeter. This limited the number of samples which could be analyzed by one operator. The CN- electrode provided a quick reading, but extra care had to be taken not to expose the electrode to a concentrated CN- solution, because the strong CN- would degrade the electrode.

Figure 5-10: Column A-2 Breakthrough (BA-7) 6/25



Source: Arthur D. Little, Inc.

## 5.3 Ion Exchange Column Regeneration

#### **5.3.1 Cation Regeneration Results**

Regenerations were performed at varying acid and rinse flow rates to determine:

- The shape of the CdSO<sub>4</sub> elution curve;
- Percent recovery of Cd<sup>2+</sup>; and
- Acid and rinsewater requirements.

5.3.1.1 Cadmium Sulfate Elution Curve. Table 5-6 summarizes the results of the cation regeneration runs RC-1 through RC-9 which were conducted to determine the effect of the acid flow rate on the shape of the CdSO<sub>4</sub> elution curve. The starting point is defined as the BV of total throughput at which the Cd<sup>2+</sup> concentration reaches 500 mg/L, and the end point is the point where the concentration falls below 500 mg/L. Both the starting and ending points were determined graphically from the regeneration curves.

During these first nine regenerations, samples of the column effluent were taken every 5 to 10 minutes resulting in a chromatographic type curve (elution curve) indicating when the majority of the Cd<sup>2+</sup> was recovered. Knowing the dimensions of the elution curve allowed for the collection of the most concentrated portion of the eluate for processing in the ERU. These curves indicated that the lower regeneration flow rates resulted in a slightly narrower Cd<sup>2+</sup> elution curve, but was generally between 1.5 to 3.0 BV of total throughput (both acid and slow rinse). These recovery peaks were not used to calculate cadmium recovery because of the errors introduced by the high weighing of the peak concentration and the potential for missing the peak concentration within the 5 to 10- minute intervals. Appendix B includes the regeneration curves except for Regenerations RC-1 and RC-2. The data collected for these two runs was insufficient to plot the curves. Figure 5-11 is a typical regeneration curve generated using this procedure.

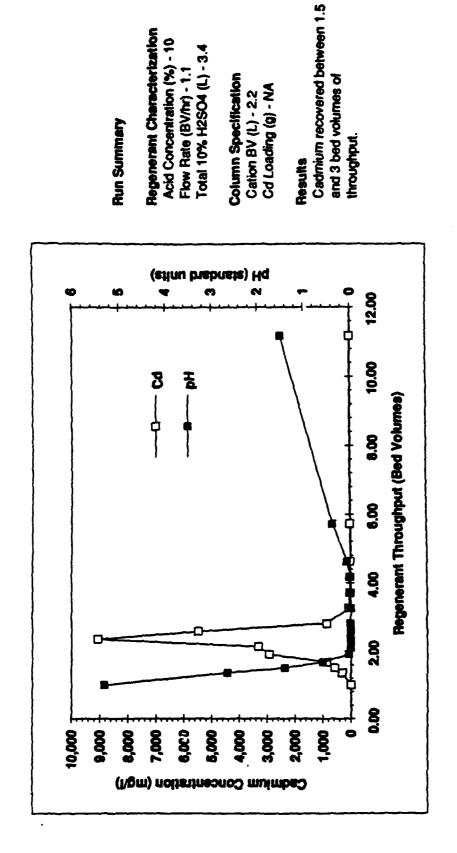
**5.3.1.2 Cadmium Recovery.** Table 5-7 summarizes the results of Regenerations RC-10 through RC-17 which provided information on Cd<sup>2+</sup> recovery. These curves were generated using a different sampling method in which all of the cluate was collected in sequenced one-liter bottles. This method of sampling provided for accurate accounting of all Cd<sup>2+</sup> removed from the column, allowing a mass balance to be calculated. The sum of the Cd<sup>2+</sup> concentration in each one-liter bottle (reported in mg/L) represents the total mg of Cd<sup>2+</sup> recovered. The total amount of Cd<sup>2+</sup> recovered during regeneration was compared with the amount loaded onto the column (which was calculated from the breakthrough curve - Section 5.2.1.1).

Table 5-6: Summary of Regenerations for Cation Columns

				B	generant C	Regenerant Characterization		Cadmium Elution	Elution
Regen Run #	Column Numiber	Regen Date	Operating Run #'s (Prior/Next)	Bed Volume (L)	Acid Cone. (%)	Acid Acid Flow Conc. Rate (%) (BV/hr)	Acid Volume (BV)	Start (BV)	End (BV)
RC-1	ទ	4/11/92	BC-1/BC-2	1.2	10	4.0	3.2	1	ı
RC-2	C-2	4/13/92	BC-1/BC-2	1.2	10	4.0	2.3	ł	1
RC-3	ઢ	4/16/92	BC-2/BC-4	1.2	01	5.0	2.3	~	ĸ
RC.▲	C-2	4/16/92	BC-2/BC-5	1.2	01	03	3.3	١	i
RC-5	ဗ	4/16/92	BC-3/BC-5	1.2	10	4.0	2.0	1.5	4.5
RC-6	2	5/15/92	BC-4/BC-6	2.2	0	1.	1.7	1.6	2.4
RC-7	င်	5/14/92	BC-5/BC-7	2.2	5	1.1	1.5	<b>6</b> .	3.2
AC-8	C-5	5/16/92	BC-5/BC-7	2.2	0	2.2	1.6	<b>8</b> .	2.4
RC-9	?	6/11/92	BC-6/BC-8	2.2	10	0.5	1.4	1.0	2.2

Source: Arthur D. Little, Inc.

Figure 5-11: Column C-3 Regeneration (Run RC-7) 5/15



Source: Anthur D. Little, Inc.

Table 5-7: Summary of Regeneration Recoveries for Cation Columns

					Regenerant Ch	eracterization		Š	Cadmium Elution	£
200 m	Cotumn	2 2 3 a a	Operating Run 8's	Bed Volum	Acid Conc.	Acid Flow	Acid Volume		Recovered	Recovery
			(Prior/Next)	(L)	(%)	(BV/hr)	(8V)	(0)	(6)	Z
RC-10	C-2	6/12/92	BC-7/BC-9	2.2	9	2.7	2.3	æ	24	æ
RC-11	ន	6/15/92	BC-7/BC-10	2.2	9	2.2	2.2	1	13	I
RC-12	5	6/20/92	BC-8/BC-11	2.2	10	2:2	1.5	24	29	8
RC-13	3	6/24/92	BC-9/BC-13	2.2	9	2.2	1.5	\$6	2	8
RC-14	3	6/24/92	BC-10/Not Used	2.2	9	2.7	1.5	ı	ន	1
RC-15	5	6/25/92	BC-11/BC-12	2.2	0	2.7	6.	ß	8	112
RC-16	 5	7/22/92	BC-12/Not Used	2.2	<b>6</b>	2.7	7.	5	SS	8
RC-17	62	7/23/82	BC-13/Not Used	2.2	10	2.7	1.4	ß	42	67

Source: Arthur D. Little, Inc.

The percent recovery indicated in Table 5-7 is satisfactory for most runs, between 73 to 112. Regeneration RC-12, which corresponds to Breakthrough Run BC-8, has an unexplained recovery of 160. The error is attributed to the graphical method of calculating Cd<sup>2+</sup> loading onto the column. As described in Section 5.2.1.3, Operational Difficulties, the recoveries calculated for the city water runs take into account the Cd<sup>2+</sup> loaded onto the column at the feed concentration and not the level where the effluent concentration leveled off. If this Cd<sup>2+</sup> loading were not accounted for, the error in recovery would be very high. The elution curves for Runs RC-10 through RC-17 are presented in Appendix B. Figure 5-12 is a typical regeneration curve using the previously described sampling procedure.

The cations that are removed from the city water along with the Cd<sup>2+</sup> are also present in the cluate, as shown in Table 5-8. These additional cations will not interfere with the recovery of the Cd via electrolytic recovery; Cd is the only metal which will be reduced to its metallic state during the process and will therefore be recovered selectively. In order to reuse the acid, a bleed stream would be required to maintain the acid concentration and to maintain the salt concentration and to keep it from interfering with subsequent regenerations.

5.3.1.3 Acid and Water Requirements. Sulfuric acid and rinsewater requirements were also derived from the regeneration runs. The results indicate that regeneration requires 1.4 to 1.8 BV of 10% sulfuric acid, which is within the manufacturer's recommended 0.9 to 1.8 BV of 10% acid. Slow rinsewater requirements averaged 3 BV followed by 14 BV in the fast rinse. The NaOH requirement is approximately 2 BV of a 5% solution, which is slightly more than the manufacturer's recommendation of 1.1 BV. The final fast rinse required approximately 14 BV of water.

#### 5.3.2 Anion Regeneration Results

Regenerations were performed at varying sodium hydroxide and rinse flow rates to determine:

- The shape of NaCN elution curve;
- Percent recovery of CN-; and
- Water/rinsewater requirements.

5.3.2.1 Sodium Cyanide Elution Curve. Table 5-9 summarizes the results of the Regenerations RA-1 through RA-5 which were used to determine the shape of the NaCN elution curve. The starting point is defined as the throughput at which the CN-rises above 100 mg/L and the end point when the concentration drops below 100 mg/L. During these regenerations, samples of the column effluent were taken every 5 to 10 minutes resulting in a chromatographic type curve. This procedure indicated that the

Figure 5-12: Column C-1 Regeneration (Run RC-16) 7/22

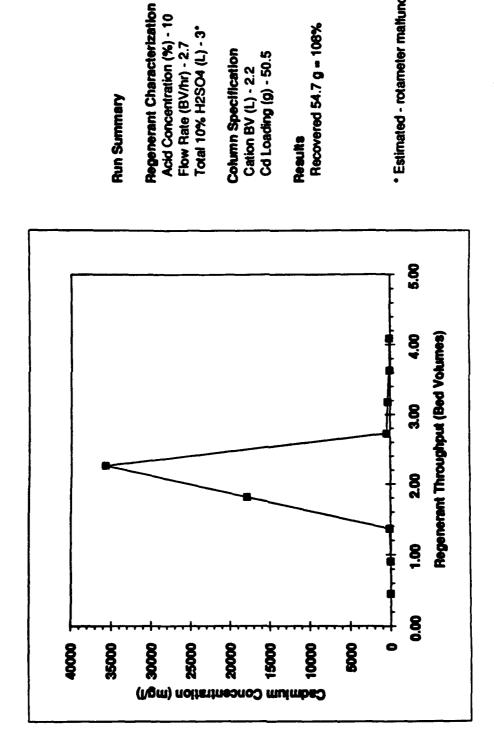


Table 5-8: Typical Cation Column Regeneration (C-3, Regeneration Run Rc-3, City Water)

Elapsed Time (min)	Volume Throughput (L)	Cd 2+	Concentratio	n (mg/L) Ca 2+
35	2.90	5800	88	930
40	3.40	6400	]	
50	4.40	3700	64	700
60	5.40	340		
65	7.40	33	1500	600
70	9.40	19	İ	
75	11.40	14	800	400
80	13.40	8		
<b>8</b> 5	15.40	11	1700	390

Table 5-9: Summary of Regenerations for Anion Columns

						<b>Service Series</b>		Cyanide Elution	
5			Operating	M Volume	Caustic	Caustic Caustic Flow (			
Bun & Number		ied	Run #'s	3	Const	Rate / rev/het	Volume (RV)	Start	
			(Prior/Next)		R	Taning!			
RA-1	<u>-</u>	4/13/92	BA-1/BA-2	2.5	ın	2.4	0.0	!	l
RA-2	A-2	4/13/92	BA-1/BA-2	2.5	us	2.4	I	1	ł
RA-3	<b>}</b> -1	4/15/92	BA-2/BA-4	2.5	S	4.1	I	1	I
₩ ₩	A-2	4/15/92	BA-2/BA-4	2.5	w	3.8	1.2	<b>-</b>	N
	6-4		BA-3/Not Used	2.5	S	2.4	1.0	1.5	2.5

Source: Arthur D. Little, Inc.

majority of the CN- is recovered in 1.0 to 2.5 BV of total throughput volume (NaOH solution and slow rinse). Figure 5-13 is a typical regeneration curve generated from samples taken every 5 to 10 minutes. Appendix C includes the regeneration curves for RA-1, RA-4, and RA-5. Runs RA-2 and RA-3 are not presented because insufficient data were obtained to develop a curve.

**5.3.2.2 Cyanide Recovery.** Table 5-10 summarizes the results of the anion regeneration runs RA-6 through RA-10. All of the regenerant was collected in sequenced one-liter bottles. This procedure provided an accurate accounting of all the CN- removed from the column enabling a mass balance to be calculated. The total amount of CN- recovered was compared with the amount loaded onto the column which was calculated from the breakthrough curve (Section 5.2.2).

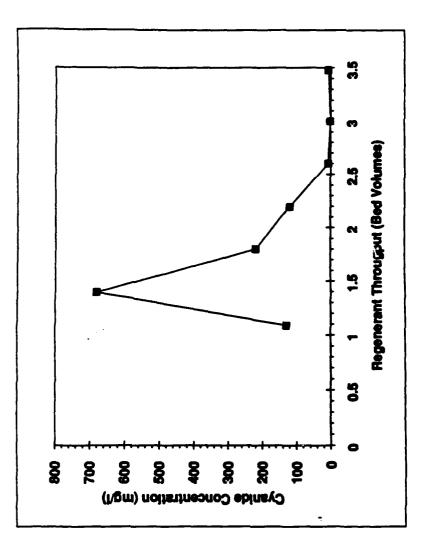
The recovery indicated in Table 5-10 is below 15% for all runs. This is attributed to the low affinity of the anion resin for CN- which allows the bound CN- to be removed from the resin during operation and during rinsing of the resin before regeneration. Another problem could be in the analysis of these high concentrations of CN- which is known to be difficult because of the need for large dilutions. Regeneration curves for runs RA-6 through RA-10 are presented in Appendix C. Figure 5-14 illustrates a typical regeneration curve using this sampling procedure.

The anions that are removed from the wastewater along with the CN- are also present in the cluate as shown in Table 5-11. These additional anion species cannot be removed from the cluate. If the cluate is recycled to the plating bath, the other anion species will also be returned to the plating bath. The estimated cluate solution concentration would be approximately 460 mg/L of CN-, 620 mg/L SO<sub>4</sub><sup>2</sup>-, 640 mg/L Cl-, and 80 mg/L of CNO-. Because the plating bath normally has CN- concentrations of 25,000 to 30,000 mg/L, the addition of the CN- cluate would greatly reduce the concentration of CN- in the plating bath, and the recycle of the cluate contaminants to the plating would result in an unsatisfactory plating bath chemistry. Because of the low concentration of CN- and the contaminants in the cluate, the CN- cluate stream is not recommended for recycle to the plating bath.

#### 5.4 Electrolytic Recovery of Cadmium

Electrolytic recovery is used to plate a metal from solution to its metallic state on a cathode. This technology can be utilized to recover metals from solution for reuse in the original plating process. The objectives in conducting the electrolytic recovery runs was to evaluate the efficiency of Cd metal recovery from the sulfuric acid eluate from the cation exchange columns.

Figure 5-13: Column A-2 Regeneration (Run RA-4) 4/15



Run Summary

Regenerant Characterization Caustic Concentration (%) - 5 Flow Rate (BV/hr) - 3.8 Total 5% NaOH (L) - 2.9

Column Specification Anion BV (L) - 2.5 CN Loading (g) - NA Results
Cyanide recovery between 1 and 2.5 bed volumes of threaghput volume.

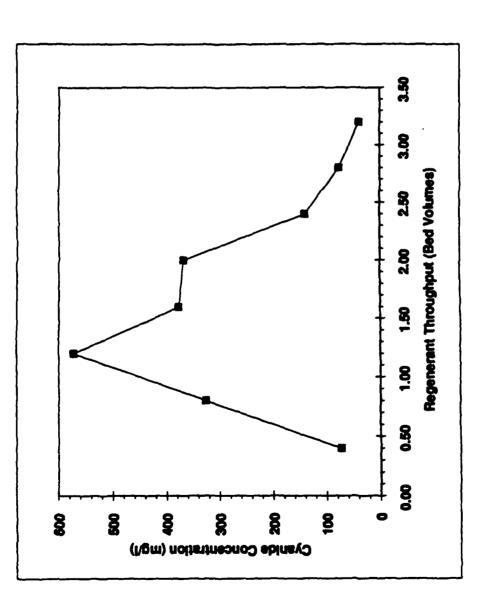
Source: Arthur D. Little, Inc.

Table 5-10: Summary of Regeneration Recoveries for Anion Columns

Regen	Column	Column Regen Operating Number Date Run Fe	Operating Bun #s	Bed Volume	Regenerant Characterization Caustic nustic FI Conc. Rate	acterization ustic Fit Rate (BV/hr)	Caustic Volume (BV)	Conding Cya	Cyanide Elution CN CN coding Recovered (a)	S See
RA-6	A-1	6/18/92	6/18/92 BA-4/BA-5	2.5	2	3.8	1.5		2.1	ł
RA-7	A-2	6/18/92	BA-4/BA-7	2.5	ß	3.8	4.	ı	1.9	ı
RA-8	¥	6/23/92	BA-5/BA-6	2.5	ĸ	2.4	1.3	17	2.5	15
RA-9	A-1	6/25/92	A-6/Not Use	2.5	s.	2.4	1.2	88	3.7	5
RA-10	A-2	6/26/92	6/26/92 A-7/Not Use	2.5	ယ	2.4	1.2	27	3.2	12

Source: Arthur D. Little, Inc.

Figure 5-14: Column A-1 Regeneration (Run RA-6) 6/18



Source: Arthur D. Little, Inc.

Regenerant Characterization Caustic Concentration (%) - 5 Flow Rate (BV/hr) - 3.8 Total 5% NaOH (L) - 3.7

Column Specification Anion BV (L) - 2.5 CN Loading (g) - 18.2 Recovered 2.1 g = 12%

Table 5-11: Typical Anion Column Regeneration (A-1, Regeneration Run RA-9, City Water)

Regenerant		Concentration	on (ma/L)	
Volume (L)	ä	804 2-		CNO -
1	98	7	124	15
2	555	556	728	52
3	795	769	1060	215
4	1192	1772	1080	129
5	604	1566	1050	136
6	402	282	905	70
7	73	29	125	13
8	30	10	33	6

To recover Cd metal from the sulfuric acid eluate, a 1.5-gallon capacity unit was set up with a peristaltic recirculating pump. The approximate cathode area is 1 square foot. The pump suction was taken from the concentrated CdSO<sub>4</sub> Tank T-4 and discharged into the ERU. The ERU overflow was piped back into T-4. The system was operated in a batch mode and only when supervised. Approximately ten gallons of eluate solution was required to fill the ERU and its associated piping while still providing sufficient reservoir for the pump to draw on. Several regenerations of the cation columns were performed before enough solution was collected. Because of the large number of runs needed to collect a sufficient volume of eluate to operate the ERU, only one ERU run was conducted.

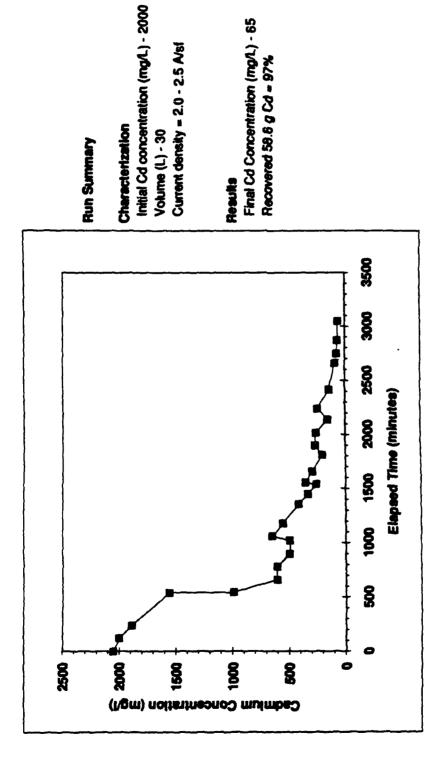
Figure 5-15 is a plot of the Cd<sup>2+</sup> concentration vs. time for the ERU run using concentrated cation resin eluate. The plot indicates a 72% removal of Cd<sup>2+</sup> in the first 8 hours, followed by an asymptotic curve for the removal of the remainder. A total of 97% of the Cd was recovered from the concentrated solution as metallic Cd for potential recycle back to the plating operation.

During the operation of the unit, hydrogen bubbling was evident at the ERU's cathode indicating that the current was set too high, above the limiting current  $(I_L)$ . Hydrogen gas evolution was further enhanced by the extremely high concentration of  $H_3O^+$  ions (low pH, approximately 0) in the solution. The high concentration of  $H_3O^+$  ions compared to  $Cd^{2+}$  ions favored hydrogen evolution. The bubbling of hydrogen affects the quality of the Cd metal plate by hindering the ability of the Cd metal to coat the cathode evenly. As a result the Cd metal that plated onto the cathodes was very dark and powdery. Consequently, it is the desirable in the operation of the ERU to minimize the amount of hydrogen generated.

An estimate of the limiting current ( $I_L$ ) was made assuming that the boundary layer thickness was approximately 5 mm. The resulting  $I_L$  was calculated to be 0.03A (3.4 x  $10^{-5}$  A/cm<sup>2</sup>). The current applied to the system was 2.5 A (2.7 x  $10^{-3}$  A/cm<sup>2</sup>), which is about eight times the  $I_L$ . It is desired to operate the system below  $I_L$ ; this can be accomplished by operating at lower current densities, or by altering the process parameters to increase  $I_L$ . The calculated current efficiency, based on the removal of 58.6 g of Cd<sup>2+</sup> metal and Faraday's law was 22%. Most of the current thus went to forming hydrogen gas.

The sulfuric acid solution remaining after electrolytic recovery processing contained approximately 65 mg/L of Cd<sup>2+</sup>. The pH was still below 0, and the concentrations of Na+ and Ca<sup>2+</sup> ions were high estimated to be 15,000 mg/L and 9000 mg/L, respectively. The high levels of these ions make the reuse of this solution as a regenerant unacceptable unless a 10% bleed stream is taken and replaced with fresh acid. In contrast, if the 10% sulfuric acid solution were made up with RO water, a 5% bleed stream would be adequate for controlling salt build-up. The recovered sulfuric acid

Figure 5-15: ERU Recovery of Cadmium from Concentrated Cation Eluate Solution



from the ERU was not used in an actual regeneration during the pilot test program, as the solution was inadvertently transferred from the holding tank by North Island personnel for disposal.

The ERU test results indicate that electrolytic recovery is a viable option for recovering the Cd<sup>2+</sup> as Cd metal from cation eluate solutions. A number of modifications, however, can be made to improve the efficiency of the process and the quality of the deposit. These include: increasing the agitation rate to decrease the boundary layer thickness and increase I<sub>L</sub>; increasing the pH to 3-4 to minimize hydrogen formation; lowering the current density; increasing the surface area; and additing certain organic compounds to improve the quality of the deposit. However, if it is desired to reuse the acid solution for additional cation column regenerations and the pH is raised for better electrolytic recovery, additional fresh acid would then have to be added to lower the pH to meet specifications for regenerant solution.

The ERU test results indicate that the use of electrolytic recovery to recover Cd metal from cation resin eluate solutions is viable. Certain process parameters can be varied to optimize the quality of the Cd deposit, to enable the recovered Cd to be recycled back to the plating process.

## 6.0 Full-Scale System Design

In preparing the design for the full-scale ion exchange system and subsequently developing capital and operating costs, we used the plating operations at the Naval Aviation Depot (NADEP) in North Island, CA, as the design basis (Table 6-1).

Based on the results of the pilot test program as outlined in Chapter 5.0 of this report, it was assumed that the recovered Cd metal could either be reused in the electroplating process or sold to an outside vendor for the full-scale design. It was also assumed that the recovered CN- could not be reused, in fact, it was assumed that anion exchange would not be utilized at all for the treatment of CN- in the rinsewaters; rather, the rinsewater containing CN- would be treated by alkaline chlorination at the existing IWTP.

As the results of the pilot test program show, ion exchange, coupled with electrolytic recovery can be applied to treat rinsewater and in conjunction with a point source treatment such as electrolytic recovery. We have developed two treatment options, either of which can be applied to treat Cd-CN rinsewater or electrolytically treated rinsewater. A detailed description of the operation of each system along with its advantages and disadvantages is provided below.

## 6.1 Cd-CN Rinsewater Treatment System Description

The Cd-CN rinsewater treatment system includes cation exchange for the removal of Cd<sup>2+</sup> from the rinsewater, followed by conventional alkaline chlorination for treatment of cyanide at the existing IWTP. This system uses the heavy metal selective cation exchange resin to break the Cd-CN complex and retain the Cd<sup>2+</sup> on the cation resin, where it is later recovered in a sulfuric acid eluate stream. After the removal of the Cd<sup>2+</sup>, the CN- is either concentrated by a reverse osmosis (RO) unit and destroyed in the IWTP alkaline chlorination system, or sent directly to the alkaline chlorination system. The treated rinsewater is then either discharged to the IWTP, or recycled back to the rinse tank.

The acid eluate from the cation columns has a  $Cd^{2+}$  concentration of 0.1 to 0.2%, and is recovered from the eluate in an electrolytic recovery unit. The  $Cd^{2+}$  is plated out of the solution, and the  $H_2SO_4$  is reused in the next regeneration step. Approximately 10% of the recovered  $H_2SO_4$  is assumed discarded to the IWTP to prevent build up of dissolved solids that may reduce the regeneration efficiency. The size of this bleed stream may require alteration based on operational experience and is dependent upon the level of dissolved solids which can be tolerated in the ERU. The amount of dissolved solids entering the system would have to be purged from the system in the bleed stream in order to maintain a constant concentration.

Table 6-1: Rinsewater Characterization for NADEP North Island

Design Throughput

Plant Operation Basis 24 hr/day (2 hours for switching and reserve

1000 gal/day

capacity)
7 days/week
52 weeks/year

# Rinsewater Composition\*

Constituent	With RO Treatment	Without RO Treatment
Cd	30 mg/l	30 mg/l
	10 eq/day	10 eq/day
CN	75 mg/l	75 mg/l
	54.5 eq/day	54.5 eq/day
Na	175 mg/l	225 mg/l
	144 eq/day	185.1 eq/day
Ca	ND	70 mg/l
	0 eq/day	66.2 eq/day
Mg	ND	30 mg/l
J	0 eq/day	47.3 eq/day
CO <sub>3</sub> 2-	100 mg/l	75 mg/l
•	63.0 eq/day	47.3 eq/day
SO₄2-	5 mg/l	275 mg/i
<del>-</del>	1.89 eq/day	108.4 eq/day
Cl-	70 mg/l	185 mg/l
	37.3 eq/day	98.6 eq/day
pН	10.5 s.u.	9.5 s.u.
Total Cation Loading		308.6eq/day 308.8eq/day

<sup>\*</sup>Based on rinsewater analyses at NADEP North Island during the pilot testing phase. ND denotes Not Detected.

After completion of the acid regeneration, the cation columns are neutralized with NaOH. The NaOH solution from the column is collected, adjusted to the correct level of NaOH, and reused for the next neutralization step. Approximately 10% of the recovered NaOH is assumed discarded to the IWTP to prevent buildup of dissolved solids. Again, this bleed stream may require alteration based on actual operating experience.

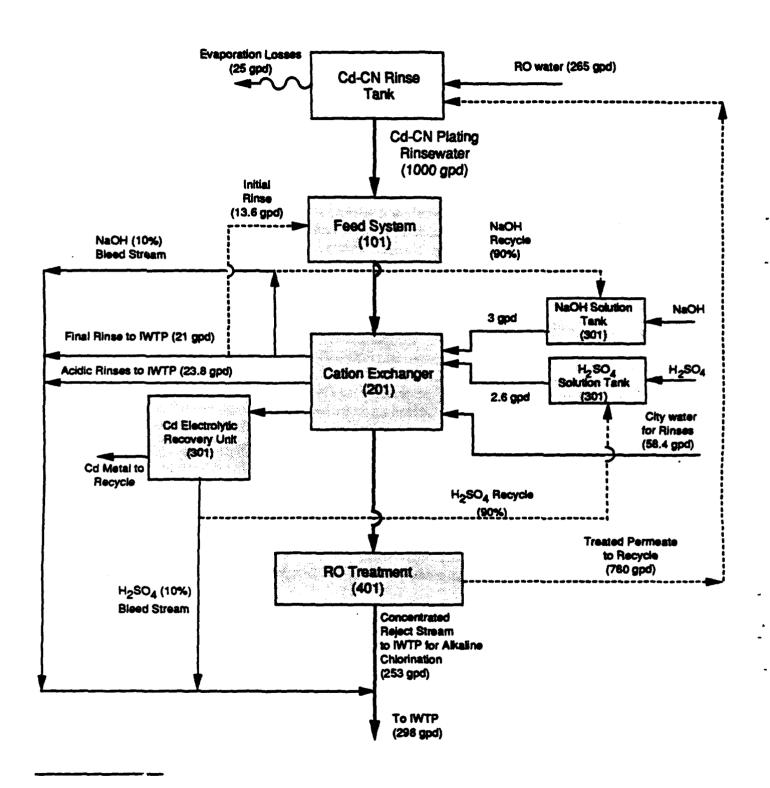
The initial rinse of the spent cation columns is recycled back to the feed tank. The rinses from the cation columns following acid regeneration are assumed to be sent to the IWTP for pH adjustment. It is possible that these rinses could be collected and be utilized following another acid-based process. Some of the rinsewater may require further processing via ion exchange due to low levels of Cd<sup>2+</sup> present. Adjustment of the pH would be required prior to returning the acidic water to the feed tank which will contain cyanide. The final rinse after NaOH neutralization is sent to the IWTP for pH adjustment.

Two possible system configurations have been developed both of which are assumed to treat 1000 gpd of rinsewater and require regeneration every 5 days. Figure 6-1 is a block flow diagram of Option No. 1 which includes RO treatment of the effluent from the cation exchanger. The RO system concentrates the CN- into a smaller volume which can then undergo alkaline chlorination at the IWTP. The treated water discharged from the RO system can then be reused in the Cd-CN rinse tank. The advantages to this system include reduced water volume discharged to the IWTP (approximately 75% less than Option No. 2), and reduced cation loading to the ion exchange columns resulting in a higher Cd<sup>2+</sup> resin capacity and a more concentrated eluate stream. This option also assumes that the makeup water used in the rinse tank is also water processed through an RO unit.

Figure 6.2 illustrates Option No. 2, which does not utilize RO to concentrate the cyanide stream (cation exchanger effluent). Instead, this stream undergoes alkaline chlorination at the IWTP. This system will require a larger volume of cation resin due to the increased cation loading of the untreated city water used in the rinse tank. This system will also discharge a higher volume of water to the IWTP, since no water is recycled.

As supported by the results of the pilot test program, no anion exchange system is included in either of these options since the concentrated NaCN, which would result from anion resin regeneration, is not of suitable concentration or quality to be recycled back to the plating bath. Therefore, the advantage of using ion exchange for the removal of CN-is voided, and a conventional treatment process is more appropriate. For this analysis, it is assumed that the CN- bearing waters exiting the cation exchange system will be treated in a two stage alkaline chlorination process. The North Island facility has such a system incorporated into their existing IWTP.

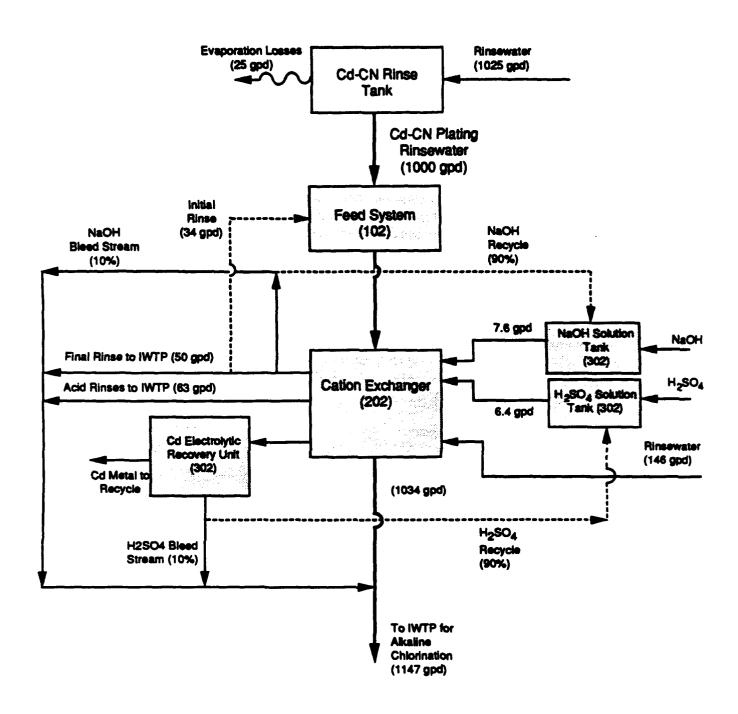
Figure 6-1: Block Flow Diagram for the Full-Scale Cadmium Cyanide Treatment - Option No.1



NOTE: Regeneration rinse volumes are averaged to a gallon per day volume, based on regeneration sequences being performed once every five days.

- System included in full-scale design and capital cost estimate.

Figure 6-2: Block Flow Diagram for the Full-Scale Cadmium Cyanide Treatment - Option No. 2





- System included in full-scale design and capital cost estimate.

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6-5

## 6.2 Design Considerations

As previously discussed, two alternatives for the Cd-CN treatment system have been developed: Option No. 1 in which the partially treated water from the cation exchange system is treated via RO, the permeate is recycled while the concentrated brine undergoes alkaline chlorination for the destruction of CN-; and Option No. 2 in which the partially treated water from the cation exchange system is discharged directly to the IWTP where it will undergo alkaline chlorination for cyanide destruction. Both systems are sized to operate for 5 days before regeneration is required treating approximately 1000 gpd. The primary difference between the two options is the quality of the Cd-CN rinsewater being treated which affects the resin Cd2+ capacity. Option No. 1 allows for high quality water from the RO system to be used as makeup for the Cd-CN rinsewater tank and assumes a resin Cd<sup>2+</sup> capacity of 485 meg/L. In contrast, Option No. 2 (which does not include an RO system) must rely on city water (lower quality, containing high concentrations of dissolved solids) for makeup water for the Cd-CN rinsewater tank. As a result, these high concentrations of dissolved solids reduce the capacity of the ion exchange resin for Cd<sup>2+</sup> as indicated in the results of the pilot test program. The assumed resin Cd<sup>2+</sup> capacity for Option No. 2 is 148 meg/L. In addition, the volume of water requiring discharge to the IWTP is much higher in Option No. 2 compared to Option No. 1. With the exception of the RO unit, these two systems are similar and have been divided into subsystems as shown below:

- System 100 Feed System;
- System 200 Cation Exchange;
- System 300 Carion Regeneration and Electrolytic Recovery; and
- System 400 Reverse Osmosis.

The design considerations for each of the subsystems are described in the following sections. Detailed equipment lists for each subsystem can be found in Appendices F and G.

# 6.2.1 Feed System - System 100

The feed system consists of a surge tank to collect the gravity discharge from the process rinsewater tank, a transfer pump for transferring the rinsewater from the surge tank to the feed tank, and a process pump to transfer the wastewater to the cation exchange treatment system. The transfer pump is designed to transfer 1,000 gallons of rinsewater per day and is equipped with a strainer at the suction of the pump. The transfer pump is constructed of epoxy coated or rubber lined carbon steel and the piping and filter housing are polyvinylchloride (PVC). The pump is controlled by the level in the surge tank which is a 250 gallon tank constructed of high-density polyethylene (HDPE). The tank provides

approximately one hour of surge capacity for the stream at an assumed rinse flow rate of 3 gpm.

From the surge tank the wastewater is pumped to the main feed tank. This feed tank is cone bottomed and constructed of HDPE with a capacity of 750 gallons for Option No. 1 and 1,000 gallons for Option No. 2. This tank provides approximately 4 hours of rinsewater holding capacity and additional freeboard to receive the regeneration rinsewaters that are recycled back to this tank. From the feed tank, the water is pumped to the treatment system. The feed pump is designed to deliver a 3 to 10 gpm with sufficient head to overcome the flow resistance in the downstream equipment. The feed pump and its installed spare are made of epoxy coated carbon steel or other chemically compatible material and are provided with duplex polypropylene cartridge filters on the pump discharge.

Figure 6-3 presents a process flow diagram for the feed system. The feed system for both Option Nos. 1 and 2 are similar, however, Option No. 2 requires a larger feed tank (T-2). In addition, Option No. 2 will require more frequent changing of the cartridge filters because of the precipitated solids characteristic of using city water.

#### 6.2.2 Cation Exchange System - System 200

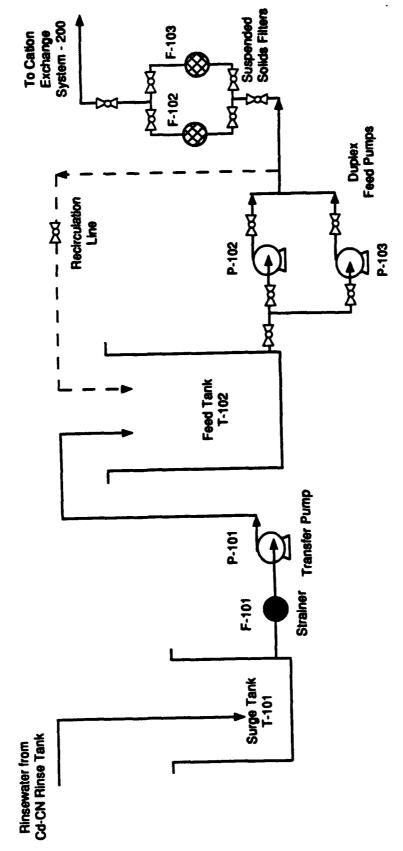
The cation exchange system is designed to operate with two columns in series for Options No. 1 and No. 2 with an additional column in standby. The standby column will be brought on-line as the polish column when the lead column breaks through. The column that has broken through will then be regenerated and placed in standby until needed. This is consistent with the design of the pilot system.

The columns for Option No. 1 are designed to hold 1.0 cubic feet of Rohm and Haas Amberlite<sup>TM</sup> IRC-718 heavy metal selective cation exchange resin, and will hold 2.5 cubic feet for Option No. 2. The resin is assumed to have a Cd<sup>2+</sup> capacity of 485 meq/L for Option No. 1 and a Cd<sup>2+</sup> resin capacity of 148 meq/L for Option No. 2, the average capacities determined from the pilot test results. The column is constructed of carbon steel or fiber reinforced plastic (FRP) with a coating of baked phenolic resin for corrosion resistance. The columns are sized for a bed expansion of 1.5 to 2 during the backwash operation. The columns are designed to switch automatically by an adjustable timer/sequencer.

Figure 6-4 illustrates the cation exchange system for Option No. 1 and Option No. 2. The cation exchange system layout for both Option Nos. 1 and 2 are similar except the higher resin volume and larger column size required in Option No. 2.

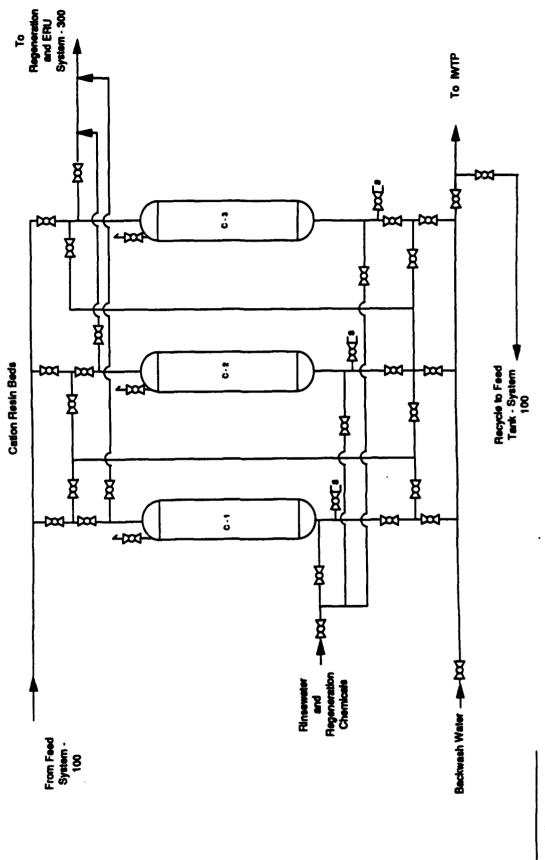
The design flow rate of 3 gpm is not constant. The rinsewater flows into the surge tank only while parts are being processed. This will result in long periods of time in which

Figure 6-3: Flow Diagram of System 100 - Feed System



Source: Arthur D. Little, Inc.

Figure 6-4: Flow Diagram of System 200 - Cation Exchange



S = Sampling Location

there is no flow through the columns while the volume of water builds up in the feed tank. During this down-time, some Cd<sup>2+</sup> may desorb from the column while attempting to achieve equilibrium. To account for this, a recycle line has been included to recycle the first 100 gallons of water from the discharge of the columns back to the feed tank (Feed System - 100). In addition, when a fresh polish column comes on line it may exhibit leakage from the regeneration step. To assure that this leakage does not create a compliance problem, the first 100 gallons of discharge from a fresh column is also recycled back to the feed tank.

# 6.2.3 Cation Regeneration and Electrolytic Recovery - System 300

When a cation column is taken off-line, the regeneration procedure is performed. An initial rinse is conducted to remove any residual CN- from the column. The acid regeneration phase is then conducted using 10% sulfuric acid stored in a 55 gallon day tank for Option No. 1 and a 150 gallon day tank for Option No. 2. A positive displacement metering pump is used to deliver the acid to the column. The concentrated Cd<sup>2+</sup> sulfate solution is stored for recovery of the Cd<sup>2+</sup> metal in solution in a 30 gallon ERU storage tank for Option No. 1 and a 50 gallon ERU storage tank for Option No. 2.

Upon completion of the acid regeneration step, the resin bed is neutralized with a 5% NaOH solution. The NaOH is delivered to the column with a positive displacement metering pump from a 55 gallon day tank for Option No. 1 and a 150 gallon day tank for Option No. 2. The concentrated NaOH discharged from the columns is collected to be reused for future neutralization of other cation columns. A minimum 10% bleed stream will be discharged to the IWTP to prevent build up of dissolved solids. A final rinse is then conducted to rinse the column of NaOH. This final rinse is discharged to the IWTP for pH neutralization.

Table 6-2 is a summary of the rinsewater volumes and chemical requirements during regeneration for both Option Nos. 1 and 2. These volumes were developed from the pilot test results and are used to determine the size of the chemical holding tanks.

The Cd<sup>2+</sup> recovery system consists of electrolytic recovery of Cd metal from the concentrated eluate solution. The ERU for Option No. 1 has a cell capacity of 12.5 gallons and for Option No. 2, 20 gallons, both of which are standard sized units. The pH of the solution is adjusted automatically by the addition of NaOH to a pH of 3 to 4. A pH probe and controller are included with the ERU. Adjustment of the pH will reduce the amount of hydrogen evolution (See Section 5.4.1) and thus improve the quality of the solid Cd metal plate. Adjustment of the pH will affect the acid concentration and will require adjustment prior to reuse as regenerant by adding fresh, 96% H<sub>2</sub>SO<sub>4</sub> or 10% solution of H<sub>2</sub>SO<sub>4</sub>. The ERU will be operated until the Cd<sup>2+</sup> concentration falls below 50 mg/l. All the Cd metal recovered will be collected and reused in the anode bags in the plating tank, or in the vacuum Cd system. The recovered sulfuric acid will be reused for additional

Table 6-2: Summary of Rinsewater Volumes and Chemical Requirements for Cation Column Regeneration

_	Flow Rate		ume	Time
Process	(gpm)	(BVs)	(gals)	(minutes)
Option No. 1 (W	ith RO Treat	tment)		
Initial Rinse	3	8	60	20
Acid Regeneration	0.125	1.8	13	104
Slow Rinse	0.125	3	22	176
Fast Rinse	3	14	105	35
NaOH Neut.	0.5	2	15	30
Final Rinse	3	14	105	35
			•	
Option No. 2 (W	ithout RO T	reatment)		
Initial Rinse	-5	8	150	30
Acid Regeneration	0.3	1.8	32	107
Slow Rinse	0.3	3	56	187
Fast Rinse	5	14	262	52
NaOH Neut.	1	2	38	38
Final Rinse	5	14	262	52

regenerations, after the acid concentration is adjusted. A 10% bleed stream is assumed to be discharged to the IWTP to prevent build up of dissolved solids in the acid solution.

Figure 6-5 illustrates the cation regeneration configuration including electrolytic recovery. The volume of the chemical holding tank plus the volume in the ERU for Option No. 1 is large enough to hold three regeneration sequences, whereas the chemical holding tank and ERU for Option No. 2 has capacity for two.

## 6.2.4 Reverse Osmosis System (RO) - System 400

Reverse Osmosis is a separation process involving the passage of pressurized water through a membrane. The characteristics of the porous membrane allow water molecules to pass through, however, dissolved solids and organic molecules are rejected. This process results in two (2) product streams: the permeate and the concentrate (reject) solution.

Typical water pressures range from 200 to 800 psi to produce a high quality permeate and a concentrated reject stream. RO process control parameters include the waste feed sentration, effective membrane surface area and the resultant flux rate across the membrane. The flux rate is largely a function of the feed concentration.

The primary process limitation is the maintenance of membrane performance. Fouling or deterioration of the membrane will reduce the flux rate and eventually require membrane replacement. RO units generally require some pretreatment to protect the membranes from solids and organics fouling. The primary pretreatment required for this application is already in place, the suspended solids filters and the cation exchange system.

The RO system for this application consists of an equalization tank from which the process pump will transfer the water to the RO membrane at high pressure. The reject or brine will be discharged directly to the CN- destruct system (at the IWTP) and the permeate will be recycled back to the process to the Cd-CN rinse tank (or other acceptable rinse tank). The design of this system revolves around two parameters; recovery rate and rejection rate. Recovery rate is the percentage of the feed which passes through the membrane as permeate. The rejection rate is the ability of the membrane to remove a particular solute material. The recovery rate for this system was assumed to be 75%, and the rejection rates vary from 92 to 98% depending upon the chemical species<sup>11,12</sup>. This recovery rate is based on vendor literature for an average case. These rejection and recovery rates would require verification prior to implementation in the form of laboratory or bench scale tests to ensure proper balancing of the flow and chemical concentration. For this application, it was also assumed that the RO system would be a single pass system treating only water from the discharge of the ion exchange treatment system and is sized accordingly.

Figure 6-5: Flow diagram of System 300 - Cation Regeneration And Electrolytic Recovery

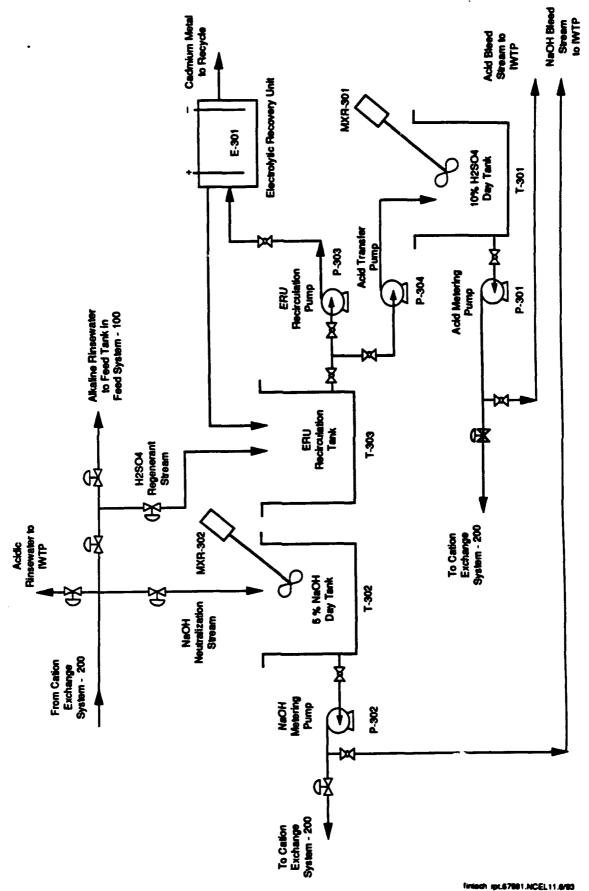


Figure 6-6 is the basic process flow and material balance for the RO system. The RO system is only included in Option No. 1. Since the quality of this water is nearly the same as the RO make up water added to the Cd-CN rinse tank, the treated water is assumed to be recycled back as rinsewater. The permeate will contain some level of cyanide, therefore, it is recommended that it be recycled back to the Cd-CN rinse tank or other CN- rinse.

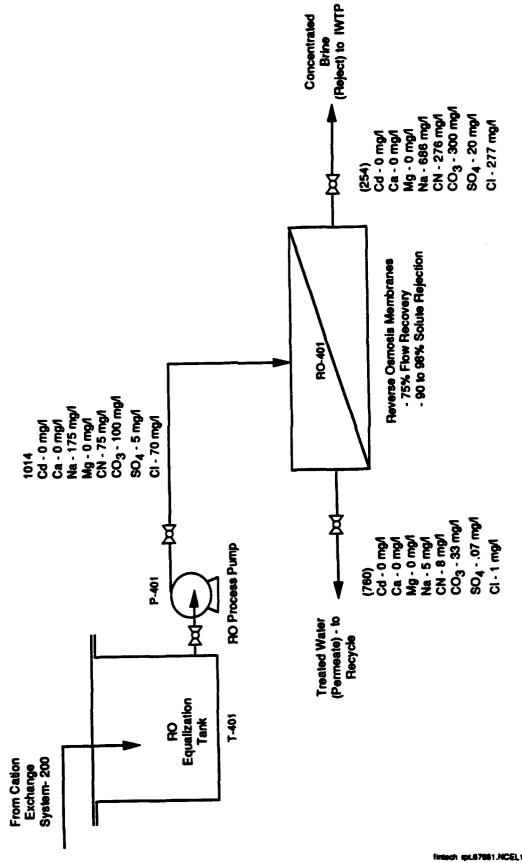
#### 6.2.5 Cyanide Destruction

The concentrated reject stream from the RO (system 400) in Option No. 1 and the discharge from the cation exchanger (system 200) in Option No. 2, is treated via alkaline chlorination in the IWTP to destroy the cyanide.

The use of alkaline chlorination for CN- destruction is a common treatment process. Under alkaline conditions, the hypochlorite oxidizes the CN- to cyanate. The pH is then reduced and additional hypochlorite oxidizes the cyanate to carbon dioxide and nitrogen. The process is conducted in two stages, each in a separate tank. The process is continuous and the reactant addition rates are regulated by pH and oxidation-reduction potential (ORP) controllers. In the first stage, the pH is adjusted to 10.5 to 11 with NaOH. Sodium hypochlorite (NaOCl) is also added to obtain an ORP of approximately +250mv. The water overflows to the second stage where the pH is adjusted to 8.5 to 9 utilizing sulfuric acid. Additional hypochlorite is added to obtain an ORP level of +600mv. North Island's IWTP has an alkaline chlorination system in place, therefore, the capital cost for such a system is not included in this report.

The same treatment technology can also be applied at the source of waste generation. If small quantities of cyanide-bearing waste are generated, the cyanide destruct system can be designed and operated in a batch treatment mode using the same procedure outlined above.

Figure 6-6: Flow Diagram of System 400 - Reverse Osmosis (RO) (Option No. 1 Only)



#### 7.0 Cost Estimation and Economic Evaluation

## 7.1 Cost Estimation Approach

For the development of component or subsystem costs, we used a combination of general published cost curves<sup>8</sup> and budgetary quotations from equipment suppliers. We used Guthrie's Modular Factor Method<sup>9</sup> to convert purchased component costs to installed costs. The modular factor, specific to each type of equipment, is intended to account for all direct and indirect cost elements in placing a piece of equipment into operation. These cost elements include: engineering; procurement; freight; insurance; field installation (materials and labor); safety subsystems (where required); and contingency. The specified modular factors that were used along with an equipment list and the purchased component costs are shown in Appendix E for Option No. 1 and Appendix F for Option No. 2. An explanation of this cost estimating procedure, and details of how the modular factors were developed, are presented in Appendix G.

Operating costs were developed based upon the operating requirements established in the system design and equipment sizing calculations as discussed in the Section 6.0 (Full-Scale System Design). Costs for operating materials were obtained from suppliers of such. Costs for labor and utilities were based on past experience at Naval Activities.

# 7.2 Capital Investment

The capital investment for the Cd-CN wastewater treatment system (Options No. 1 and 2) are summarized in Table 7-1 and are \$209,400 and \$206,300 respectively. The total capital cost for each option is essentially the same. The ion exchange system and the reverse osmosis system are the major costs for Option No. 1, while the ion exchange and regeneration systems are the major costs for Option No. 2. Option No. 2 requires larger columns, more resin, and larger tanks due to the poorer water quality and resulting lower Cd<sup>2+</sup> resin capacity. The result is a higher capital cost for the ion exchange and regeneration systems, which is nearly the same as the capital cost for the RO system in Option No. 1.

The development of the capital cost investment for the treatment systems was based upon vendor quotations for the ion exchange skids and auxiliary equipment. No building costs are included as it was assumed that the system would be installed in an existing building. If it is determined that additional building space is required, these costs must be added to the capital investment.

Table 7-1: Capital Investment Summary for Cd-CN Rinsewater
Treatment Systems

System Number	Description	Option No. 1 Installed Cost (1992\$)	Option No. 2 Installed Cost (1992\$)
100	Feed System	19,300	20,200
200	Cation Exchange	80,200	104,400
300	Regeneration and Electrolytic Recovery	26,200	44,600
400	Reverse Osmosis	47,800	NA
	Field Instrumentation	4,000	4,000
	Total Installed Equipment	\$177,500	\$173,200
	Additional Engineering Fee (3% of Total Installed Equipment)	5,325	5,196
	Additional Contingency (15% of Total Installed Equipment	26,625	25,980
	Total Capital Investment	\$209,500	\$204,400

NA - Not Applicable

# 7.3 Operating Costs

Operating costs for the Cd-CN wastewater treatment system (Options No. 1 and 2) are shown in Tables 7-2 and 7-3. The operating costs are divided into two categories, variable costs and fixed costs. Variable costs are those associated with cation resins, regenerant chemicals, RO membrane replacement, credit for recovered materials, utilities, operating labor, and disposal. Operating labor includes periodic shift oversight, regeneration oversight, and sampling to determine breakthrough. Fixed costs include maintenance and plant overhead. Maintenance includes labor and materials to repair equipment such as pumps, valves, the RO system, or the electrolytic recovery unit. It is estimated at 4% of the total capital cost because it is a fairly simple system and will likely not have many mechanical failures. Plant overhead covers those costs associated with payroll overhead items such as pensions, paid vacations, insurance, social security, etc, along with building overhead (including the maintenance of medical and recreational facilities, administration, purchasing, warehousing and engineering).

The total annual cost for the operation of Option No. 1 is approximately \$68,200 split almost equally between variable costs and fixed costs. The majority of the fixed costs in Option No. 1 is associated with operating labor, 84%. The annual operating cost for Option No. 2 is approximately \$71,100, again with almost an even split between variable costs and fixed costs. The contribution of the operating labor to fixed cost is slightly less than in Option No. 1 (77%) because the chemical and utility costs are higher for Option No. 2.

The operating costs for the two Options are very close, with Option No. 1 being about \$3,000 per year lower than Option No. 2. Option No. 1 requires periodic replacement of RO membranes, while Option No. 2 requires higher volumes of regenerant chemicals. The utility requirements, however, for Option No. 1 are lower than Option No. 2 because of smaller electrical equipment sizes and lower water treatment costs (approximately 75% of the water is recycled).

Tables 7-4 and 7-5 indicate the power consumption utilized to develop the electrical requirements for the operating costs for both Options No. 1 and 2. All electric motors were assumed to operate 50% of the time with an efficiency of 75% unless otherwise documented. The power requirements for Option No. 1 and Option No. 2 are similar even though Option No. 2 includes larger pumps, mixers and ERU unit. This is because of the added power requirement of the RO system in Option No. 1.

Calculations for the water balance and chemical consumption can be found in Appendix H. The calculations for water usage in Option No. 1 include a 75% rinsewater recycle which minimizes the annual water and waste water treatment costs. The calculations for chemical consumption in both Options include a 70% recovery which also minimizes costs.

Table 7-2: Operating Costs for the Cadmium Cyanide Treatment System - Option No. 1

<b>8</b>	11-14-14-0		st/Unit Dollars)	Annual Cost (1992 Dollars)
item Variable Costs	Units/Year	(1442	Dollars)	(1002 Donald)
Variable Costs				
Raw Materials				
<ul> <li>IRC-718 Cation Resin</li> </ul>	0.6 cu. ft.*		330.00	198
<ul> <li>50% Sodium Hydroxide</li> </ul>	0.21 tons		300.00	63
<ul> <li>98% Sulfuric Acid</li> </ul>	25 gals		0.20	5
<ul> <li>RO Membranes</li> </ul>	0.5 membrane**		1800.00	900
Recovered Material Credit				
Cadmium Metal	91 lbs		(2.75)	(250)
Sodium Cyanide	0 lbs		(.85)	0
Utilities				
• Electricity	47359 kW		0.06	2,842
• Water	120 1000 gals		0.50	60
Water Treatment	110 1000 gals		10.00	1,100
Labor				
<ul> <li>Operating</li> </ul>	900 hr		23.00	20,700
<ul> <li>Supervisory</li> </ul>	100 hr		30.00	3,000
Disposal	1 0 drums (55 gal	)	300.00	3,000
	Subto	tal Vai	riable Costs	\$31,617
Fixed Costs				
Maintenance				
<ul> <li>Labor and Materials</li> </ul>	4% of	Capita	i investment	8,380
Plant Overhead	119%	of Tota	i Labor	28.203
	Subto	tal Fix	ed Costs	\$36,583
Total Operation	ng Cost			\$68,200

<sup>\*</sup> Assumed to be replaced every five years.

<sup>\*\*</sup> Assumed to be replaced every 2 years.

Table 7-3: Operating Costs for the Cadmium Cyanide Treatment System -Option No. 2

item	Units/Year	Cost/Unit	Annual Cost
Variable Costs		(1992 Dollars)	(1992 Dollars)
Raw Materials     IRC-718 Cation Resin     50% Sodium Hydroxide     98% Sulfuric Acid	1.5 cu. ft.°	330.00	495
	0.6 tons	300.00	180
	60 gals	0.20	12
Recovered Material Credit	91 lbs	(2.75)	(250)
	0 lbs	(.85)	0
Utilities	52259 kWh	0.06	3,136
	420 1000 gals	0.50	210
	420 1000 gals	10.00	4,200
Labor     Operating     Supervisory	900 hr	23.00	20,700
	100 hr	30.00	3,000
Disposal	10 55 gal drun	300.00	3,000 \$34,682
Fixed Costs			
Maintenance • Labor and Materials	4%	of Capital Investment	8,176
Plant Overhead		% of Total Labor	28,203 \$36,379
Total Operating C		ividi fiaev vvsis	\$71,100

<sup>\*</sup> Assumed to be replaced every five years.

Table 7-4: Summary of Power Consumption - Option No. 1

Item	HP	Theoretical kW	Efficiency	Actual kW
P-102, P-103	2	1.49	0.75	1.99
P-301	0.75	0.56	0.75	0.75
P-302	0.75	0.56	0.75	0.75
E-301/P-303	4	2.98	0.8	3.73
MXR-301	0.25	0.19	0.75	0.25
MXR-302	0.25	0.19	0.75	0.25
RO-401/P-401	5	3.73	0.75	4.97
Total				12.68 kW

Assumptions:

System operates 24 hours per day, 7 days per week, 365 days per year. All components requiring electricity are in operation 50% of the time. Component efficiencies were estimated to be approximately 75%, unless otherwise documented.

<sup>\*</sup> The storage capacity in this unit and the holding tank is much larger than the volume of eluate generated each week. Thus it will be operated less often than the ERU unit in Option No. 2. This is accounted for in the total operating costs.

Table 7-5: Summary of Power Consumption - Option No. 2

Item	HP	Theoretical kW	Efficiency	Actual kW
P-102, P-103	2	1.49	0.75	1.99
P-301	0.75	0.56	0.75	0.75
P-302	0.75	0.56	0.75	0.75
E-301/P-303	8	5.97	0.8	7.46
MXR-301	0.5	0.37	0.75	0.50
MXR-302	0.5	0.37	0.75	0.50
Total				11.93 kW

Assumptions:

System operates 24 hours per day, 7 days per week, 365 days per year. All components requiring electricity are in operation 50% of the time. Components efficiencies were estimated to be approximately 75%, unless otherwise documented.

Labor costs are assumed to be equal for both systems. The additional labor to operate the RO system in Option No. 1 offsets the additional labor required to handle the large columns and longer regeneration sequences in Option No. 2.

It was assumed that 10 (55 gal) drums of hazardous waste per year would require disposal. This would include spent resin, used filter cartridges, concentrated solutions not allowed to be discharged to the IWTP (as occurred during the pilot test program), and wastes from on-site analysis (Hach kit wastes).

#### 8.0 Conclusions and Recommendations

The objective of the Cd-CN wastewater treatment pilot test program was to determine the feasibility of cation/anion exchange and electrolytic recovery for the treatment and recycle of Cd and CN- from actual plating rinsewater. The optimum conditions for operating the ion exchange system, observed during the laboratory phase of this study, were utilized during the pilot test program to gather insight into resin capacity, optimum regeneration conditions, process safety issues, process monitoring, emergency procedures and the performance of on-line instrumentation. In addition, the pilot study was more specifically focused on determining the ability of the cation/anion exchange system to treat the plating rinsewater at North Island NADEP. To investigate the ion exchange systems' applicability to North Island, four different types of cadmium plating rinsewater were processed, including:

- City water with low concentrations of Cd<sup>2+</sup> and CN-;
- City water with high concentrations of Cd<sup>2+</sup> and CN-;
- RO water with low concentrations of Cd<sup>2+</sup> and CN-; and
- RO water treated by an electrolytic recovery unit.

Cadmlum Resin Capacities. The cation exchange system proved to be technically capable of breaking the Cd-CN complex and removing and concentrating  $Cd^{2+}$  from all four of the plating rinsewaters. The  $Cd^{2+}$  resin capacities from pilot operations were found to be similar to the results found in the laboratory ion exchange study; varying from 75 meq/L for Run BC-2 (a city water run with low  $Cd^{2+}$  concentration and a high cation concentration) to 630 meq/L for Run BC-9 (a RO water run with a low  $Cd^{2+}$  concentration and a very low ionic strength). The pilot testing also demonstrated the same relationship between non- $Cd^{2+}$  cation concentration and  $Cd^{2+}$  concentration and  $Cd^{2+}$  resin capacity as observed in the laboratory study:

- Cd<sup>2+</sup> resin capacity increases as the non-Cd<sup>2+</sup> cation concentration of the solution decreases; and
- Cd<sup>2+</sup> resin capacity increases as the non-Cd<sup>2+</sup> cation:Cd molar ratio decreases.

The capacity of the resin for Cd<sup>2+</sup>, as predicted by the laboratory results, was shown to be affected by the cation concentration of the water being used in the plating rinse tank. The city water at NADEP North Island contains high concentrations of dissolved solids such as calcium, magnesium, and sodium which decreased the resin's capacity for Cd<sup>2+</sup>. The results showed an average Cd<sup>2+</sup> resin capacity of 150 meq/L for the city water runs with low Cd<sup>2+</sup> concentration; an average Cd<sup>2+</sup> resin capacity of 430 meq/L for the city water runs with a high Cd<sup>2+</sup> concentration; an average Cd<sup>2+</sup> resin capacity of 480 meq/L for the RO water runs; and a Cd<sup>2+</sup> resin capacity of 410 meq/L for the electrolytically treated dragout water.

The first set of city water runs, with a low Cd<sup>2+</sup> concentration, had the lowest Cd<sup>2+</sup> resin capacity because these runs on average had the highest cation concentration and the highest cation:Cd molar ratio. The second set of city water runs, with a high Cd<sup>2+</sup> concentration, had much higher Cd<sup>2+</sup> resin capacity even though the cation concentration remained constant because the cation:Cd molar ratio decreased from 60

to 30 (due to the higher Cd<sup>2+</sup> concentration). The RO water runs had a slightly better Cd<sup>2+</sup> resin capacity than the second set of city water runs because the cation concentration of the RO water runs was much lower than the city water runs; therefore, the cation:Cd molar ratio was lower, 25. The results of these three sets of runs supports the general conclusion that the Cd<sup>2+</sup> resin capacity increases as a function of the decrease in the cation concentration and the cation:Cd molar ratio.

However in contrast to the two sets of city water runs and the RO water runs, the electrolytically treated dragout water run did not correlate with the predicted results of the laboratory model. The model predicted a Cd<sup>2+</sup> resin capacity of 170 meq/L and the actual pilot plant result was 410 meq/L. The reason for the difference between the predicted and actual results is unknown.

Cation Regeneration. The regeneration of the cation columns was performed at several different flow rates over a range of 0.5 BV/hr to 5.0 BV/hr. The lower regeneration flow rates resulted in a more concentrated cadmium sulfate (CdSO<sub>4</sub>) solution eluting from the column in a smaller number of bed volumes. For a flow rate of 1.1 BV/hr and 2.2 BV/hr, the CdSO<sub>4</sub> was collected between 1.5 and 2.5 bed volumes. In addition, a flow rate of 2.2 BV/hr or less appeared to minimize leakage of Cd<sup>2+</sup> from freshly regenerated polishing columns.

In addition, the apparent recovery during regeneration ranged from 67% to 157% but averaged at nearly 100%. The concentrated portion of the regenerant stream was collected for processing in an electrolytic recovery unit (ERU) to recover the Cd<sup>2+</sup> as Cd metal. The average concentration of the eluate was approximately 1200 mg/L and included several thousand mg/L of other cations, including Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>.

The concentrated regenerant, CdSO<sub>4</sub>, was collected and processed through an ERU for recovery of Cd metal. Approximately 97% of the cadmium was recovered from the solution as Cd metal, however, the quality of the plate was poor. The quality of the plate was affected by the high current density applied, the slow agitation rate, and the extremely low pH of the solution. The calculated current efficiency was very low, 22%, indicating that almost all of the current went to forming hydrogen gas. It is likely that the recovered cadmium could be reused in the plating tank (in the anode bags) or the vacuum cadmium system if the quality of the plate were improved. To improve the efficiency and quality of the plate, process conditions would need to be altered to raise the pH and increase the agitation.

Cyanide Resin Capacities. The recovery and reuse of CN- from the plating rinsewater using an anion exchange resin was not an efficient recovery technology and was eliminated from the full-scale design for two reasons:

- The high concentration of non-CN-anions (e.g., CO<sub>3</sub><sup>2</sup>-, SO<sub>4</sub><sup>2</sup>-, Cl-) present in both the city water and the plating solution had a strong negative impact on the CN-resin capacity; and
- The low affinity of the anion resin for CN-produced a breakthrough curve where CN-quickly broke through the resin bed at the regulatory limit (within the first 20 bed volumes) and then slowly reached complete breakthrough.

Because of the high concentration of anions in the rinsewater, the OH-CN resin capacity model developed in the laboratory study was invalidated and could not be used to predict the actual CN- breakthrough. While the model was not able to predict the actual CN- resin capacity, the results did show that as the concentration of cyanide decreased the resin CN- capacity decreased as demonstrated in the laboratory study. The anion columns had an average capacity of 140 meg/L when using city water. The capacity was slightly increased to an average of 190 meg/L when utilizing RO water, however, this is still only 15% of the manufacturer's estimate of total resin capacity. The average CN- resin capacity for the electrolytically treated dragout water (RO D.O.) was 450 meg/L. This higher capacity is attributed to the higher CN- solution concentration, 180 mg/L. The total anion concentration: CN- ratio for these runs and the RO water runs are identical, indicating that CN- solution concentration has more of an effect on CN- resin capacity than does total anion concentration.

As mentioned above, the low affinity of the anion resin for CN- produced a breakthrough curve where CN- quickly broke through the resin bed at the regulatory limit and then slowly reached complete breakthrough. The swift breakthrough caused the polishing column to also reach the regulatory breakthrough rapidly; therefore, the anion columns were quickly out of compliance with the Federal Pretreatment Standards for Metal Finishers (compliance limit of 1.2 mg/L Total Cyanide [TCN] daily maximum and 0.65 mg/L average monthly for existing systems<sup>10</sup>). The effluent from the polishing column was unable to maintain this compliance level for more than a few hours after being put on-line. In order to maintain compliance for even a complete day the volume of anion resin would have to be increased by a factor of at least 10.

Anion Regeneration. Regeneration of the anion columns indicated poor recovery of the CN-. Recovery of CN- ranged from 12 to 15%, and the concentration of CN- in the solution was approximately 650 mg/L which is far below the plating bath concentration of 25,000 to 30,000 mg/L. In addition, the anions (e.g., Cl-, CO<sub>3</sub><sup>2</sup>-, SO<sub>4</sub><sup>2</sup>-) which compete with the CN- for removal by the anion resin are also removed during regeneration (some of which are considered contaminants to the plating bath). The CN-was also noted to degrade in the feed tank of the ion exchange system into cyanates (CNO-) which are also plating bath contaminants. Thus the low concentration of CN-and the presence of plating bath contaminants, make the reuse of the anion eluate in the plating bath impossible without additional processing.

Because the CN-solution cannot be reused directly in the plating bath and the anion columns are not reliable for maintaining compliance with the regulatory limits, the use of ion exchange for the treatment of CN- was not included in the preliminary design. Instead, conventional alkaline chlorination was the assumed method for treating the CN- contaminated streams exiting the cation columns.

Full-Scale Design. Based on the results of the pilot test study, full-scale designs were prepared for two treatment systems:

• Option No. 1 - Includes cation exchange for the removal of Cd<sup>2+</sup>, followed by reverse osmosis to concentrate the CN- and further treat the cation exchange effluent. The concentrated CN- stream is discharged to the IWTP where it will undergo alkaline chlorination. The treated RO water is returned to the Cd-CN rinse tank as rinsewater; and

• Option No. 2 - Includes cation exchange for the removal of Cd<sup>2+</sup>. The effluent from the cation exchanger is discharged directly to the IWTP where it will undergo alkaline chlorination.

The options differ both in the components comprising the system and also in the quality of the rinsewater. Option No. 2 assumes the use of RO water as makeup to the rinse tank. Option No. 2 assumes city water as makeup to the rinse tank. The basic characteristics of the wastewater for each of the options, with a total flow of 1,000 gallons per day, is as follows:

	Concentration (mg/l)						
Constituent	Option No. 1	Option No. 2					
Cd2+	30	30					
CN-	75	75					
Na+	175	225					
Ca2+	0	70					
Mg <sup>2+</sup>	0	30					
Mg <sup>2+</sup> CO <sub>3</sub> <sup>2-</sup>	100	75					
SO <sub>4</sub> 2.	5	275					
Ch	70	185					
pН	10.5	9.5					

Capital and Operating Costs. Upon completion of the full-scale designs, capital and operating costs were developed for both options. The costs were compared to each other to determine which system was economically favorable. The capital costs for each system are as follows:

- Option No. 1 (with RO) \$209,500
- Option No. 2 \$204,400

The annual operating costs for the two systems are:

- Option No. 1 \$68,200
- Option No. 2 \$71,100

These costs are lower than the costs developed during the conduct of the Laboratory Study<sup>6</sup> because the size of the system is smaller: 1,000 gpd for this study vs. 10,000 gpd for the Laboratory Study.

The capital cost for both systems are nearly the same. The RO system in Option No. 1 adds capital cost while the capital cost for Option No. 2 is affected by the lower resin capacity as a result of the poorer quality water requiring larger resin volume. Capital costs for both Options can be reduced (by equal ratios) if a system is specified with less

automatic controls. Such a system would require more operating labor (higher operating costs), and manual control. The capital costs for this study, however, were based upon an automated system requiring minimal operator supervision.

The operating cost associated with both systems are split almost equally between fixed and variable costs. Operating costs for Option No. 2 are higher than for Option No. 1, due to the larger chemical volumes required for resin regeneration and rinsing. In addition, Option No. 2 does not include any water recycle to the Cd-CN rinse tank, resulting in a larger volume of wastewater being discharged to the IWTP.

The capital and operating costs developed in an earlier study for a conventional metals precipitation and alkaline chlorination treatment system for a 1000 gpd system are as follows:

- Capital Costs \$115,000; and
- Operating Costs \$47,000/year

The capital costs is approximately 50% lower for the conventional system than for the ion exchange/electrolytic recovery system, and the operating costs are also lower. The hidden costs of hazardous waste generation, however, must also be examined when comparing costs.

Recommendations. Ion exchange can be applied to treat Cd-CN plating rinsewater. The use of cation exchange and electrolytic recovery is shown to be very successful as a treatment process as well as a recovery process for Cd metal. The effluent from the polishing columns was below the Federal regulatory limits for most runs (0.69 mg/L daily maximum and 0.26 mg/L monthly average). Anion exchange, however, is not recommended as a treatment and recovery option for CN- due to: the low resin capacity for CN-; the inability to maintain compliance with Federal regulatory limits; the poor quality of the concentrated regenerant; the ease of treatment of cyanide in an alkaline chlorination system; and the low cost of purchasing virgin NaCN.

In addition, the use of RO as a pretreatment process for the water feeding the rinse tank and as a treatment process to allow recycle of the treated rinsewater lowers the operating costs of the full-scale system. There are, however, several concerns associated with the treatment system that should be addressed prior to implementing a full-scale system. These concerns include the following:

- The use of pH adjustment and/or the use of additives to improve the plate quality in the ERU:
- The ability of the existing IWTP to handle the low volume, high concentration of CN- bearing waste generated by the RO unit;
- The distribution system required to recycle the treated water back to the Cd-CN rinsewater tank; and
- The level of automation desired for the system;
- Reuse of acid eluate for regeneration and the required bleed stream to maintain an acceptable level of dissolved solids; and

 Verification of the ability to properly control the RO-based ion exchange system based on breakthrough of the lead column.

#### 9.0 References

- Semmens, M.J., Chang, Y., "Selective Cyanide Recovery from Wastewater Containing Metal Cyanide Complexes," 43rd Purdue Industrial Waste Conference Proceedings, Lewis Publishers, 1989.
- <sup>2</sup> Semmens, M.J., Kenfield, C.F., Qin, R., Cussler, E.L., "The GM-IX Process: A Novel Metal Cyanide Treatment and Recovery Technique," 42nd Purdue Industrial Waste Conference Proceedings, Lewis Publishers, 1988.
- <sup>3</sup> Semmens, M.J., Kenfield, C.F., Qin, R., Cussler, E.L., "Cyanide Recovery Across Hollow Fiber Gas Membranes," *Environmental Science and Technology*, Vol. 22, No. 10, 1988.
- 4 Qin, Z., Cussler, E.L., "Hollow Fiber Gas Membranes," AIChE Journal, Vol. 31, No. 9, 1985.
- Koff, J., Zarate, D., "Draft Feasibility Report on Capacity of Selective Cation Exchange Resins for Cadmium," Unpublished, 1989.
- Arthur D. Little, Inc., "Final Feasibility Study: Cyanide Wastewater Treatment and Recovery Using Ion Exchange," Prepared for the Naval Civil Engineering Laboratory under Control No. N47408-89-D-1025, September 1991.
- Stat Options, "Economic Evaluation of Electrolytic Recovery of Cadmium Cyanide Wastewaters," Prepared for the Naval Civil Engineering Laboratory under Purchase Order Number N6258388P2544, 1989.
- <sup>8</sup> Guthrie, K. M., "Process Plant Estimating Evaluation and Control," Craftsman Book Company of America, Solana Beach, California, 1974.
- 9 Guthrie, K. M., "Data and Techniques for Preliminary Capital Cost Estimating," Chemical Engineering, March 24, 1969, pp. 114-133.
- "Guidance Manual for Electroplating and Metal Finishing Pretreatment Standards," USEPA, Effluent Guidelines Division and Permits Division, Washington, DC, February, 1984.
- Donnelly, R.G., Goldsmith, R.L., McNulty, K.M., Tan, M., "Reverse Osmosis Treatment of Electroplating Wastes", <u>Plating</u>, May, 1974.
- Personal Communication and Vendor Literature with Skip Iltis, Osmonics, Inc., Minnetonka, MN.

# Appendix A: Summary of Sampling and Analytical Procedures

Figure A-1: Sampling Matrix

NALYSIS** ISE HACH TESTS	4, Cd pH 1/day grab for CN CN, Cd, and Cd Ci, Ca, Mg.	pH 1/4 hrs for Cd sampler)	1/hour grab for Cd: pH 1/4 hrs for Cd (if automatic sampler available)	CN, pH 1/4hrs for CN sampler)	in CN, pH 2/ day for CN for TDS	None None	rab for Cd Cd, pH None	PH None	
LABORATORY ANALYSIS**	1/day grab for CN, Cd 1/batch grab for CN, Cd, Na, CO3, SO4, Cl, Ca, Mg, Fe, Cu, etc.	1/hr for Cd: (use automatic sampler)	1/hour grab for Cd: (if automatic samp	1/hr for CN (use automatic sampler)	1/day grab for CN 1/2-3 days grab for TDS	None	1/3-5 minutes grab for Cd	None	
SAMPLE LOCATON	1. Contents of Tank T-1	Effluent from lead cation column	Effluent from polishing cation column	Effluent from lead anion column	Effluent from polithing anion column	6. CATION REGENERATION Initial Rinse	Regeneration	Slow and Fast Rinse	

\*\*NOTE: Not all the collected samples were analyzed.

Figure A-1: Sampling Matrix

HACH TESTS	None			None
<b>18</b>	None	£	£	Cd. pH
LABORATORY ANALYSIS**	None	1/3-5 minutes grab for: CN	None	1/2 hours grab for Cd
SAMPLE LOCATON 7. ANION REGENERATION	Initial Rinse	Regeneration	Slow and Fast Rinse	8. ELECTROLYTIC RECOVERY OF CADMIUM

\*\*NOTE: Not all the collected samples were analyzed.

SOURCE: Arthur D. Little, Inc.

Figure A-2: Sample Collection, Preservation, and Analysis

Method Detection Limits	1.0 mg/L	0.01 mg/L	0.02 mg/L	0.01 mg/L	0.01 mg/L	1.0 mg/L	0.2 mg/L	0.01 mg/L	1.0 mg/L	1.0 mg/L	1.0 mg/L	10 mg/L
Methods	EPA 200.7	<b>EPA 200.7</b>	EPA 325.3	<b>EPA 200.7</b>	EPA 335.3	SM 4500	EPA 310.7	<b>EPA 200.7</b>	<b>EPA 200.7</b>	EPA 200.7	EPA 375.3	EPA 160.1
Holding Time	6 months	6 months	7 days	8 months	14 days	14 days	8 months	6 months	8 months	8 months	28 days	7days
Preservation	None.	None.	Cool to 4C	None.	4 to 6 pellets NaOH/ liter	4 to 6 pellets NaOH/ liter	•eroN	None	None*	None.	Cool to 4C	Cool to 4C
Container Type and Volume Required	P: 100 ml	P: 100 ml	P: 500ml	P: 100 ml	P: 1000 ml	P: 1000 ml	P: 100 ml	P: 100 m	P: 100 m	P: 100 ml	P: 100 ml	P: 100 ml
Parameters	5	8	ច	8	8	9	g	æ	2	* 2	. <b>S</b>	201

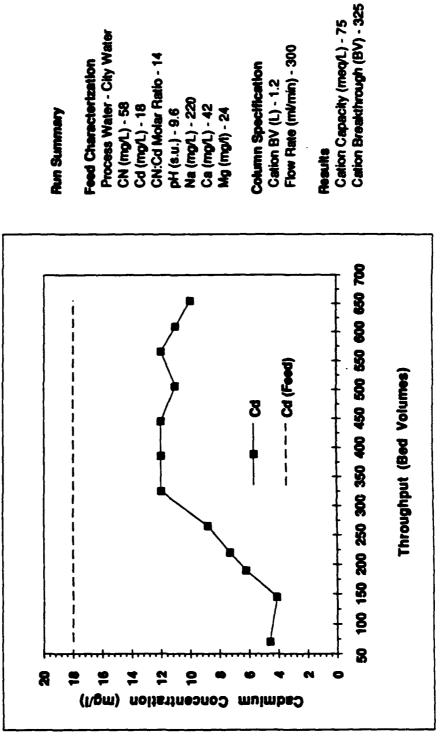
P - Plastic

EPA-600/4-79-020 Methods for Chemical Analysis of Water and Wastes Standard Methods for the examination of Water and Wastewater (17th edition) Sources:

<sup>•</sup> Due to the presence of cyanide in the wastewater, nitric acid was not added to the sample bottles in the field. pH adjustment to below 2 was conducted by the laboratory under a hood.

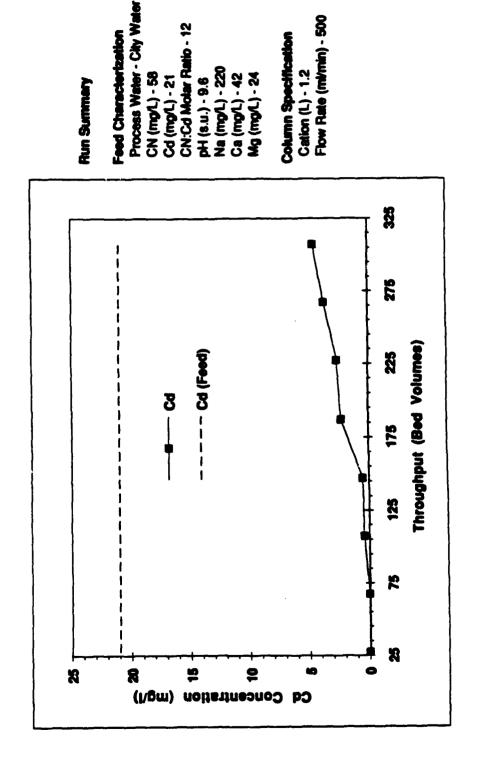
# Appendix B: Cation Column Breakthrough and Regeneration Curves

Figure B-1: Column C-1 Breakthrough (Run BC-2) 4/13-4/15



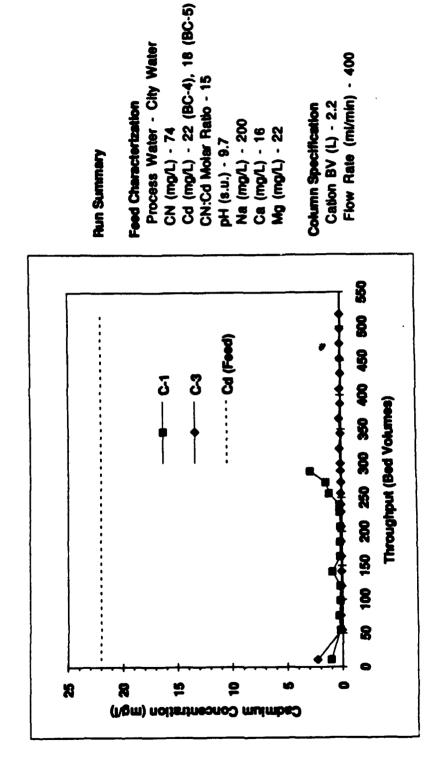
Process Water - City Water

Figure B-2: Column C-3 Breakthrough (Run BC-3) 4/15



Source: Arthur D. Little, Inc.

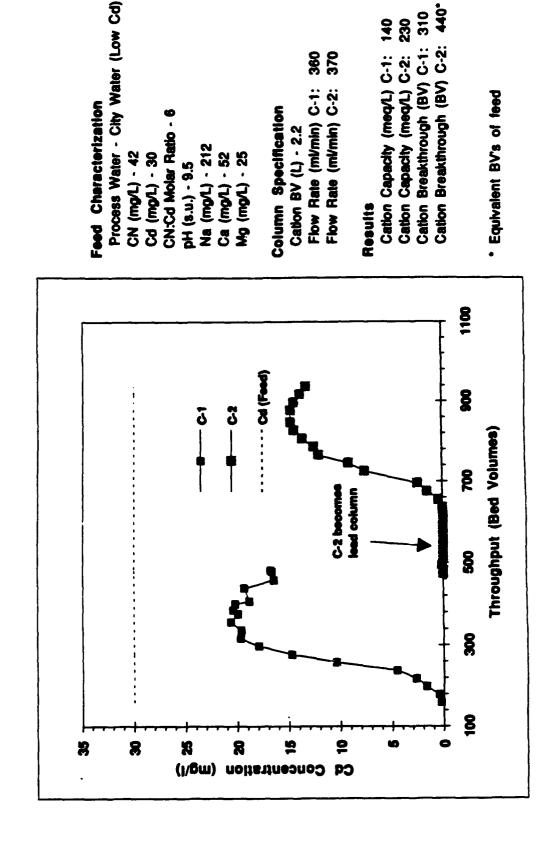
Figure B-3: Columns C-1 and C-3 Breakthroughs (Runs BC-4 and BC-5) 5/12-5/13



Source: Arthur D. Little, Inc.

**B-**5

Figure B-4: Columns C-1 and C-2 Breakthroughs (Runs BC-6 and BC-7) 6/8-6/11

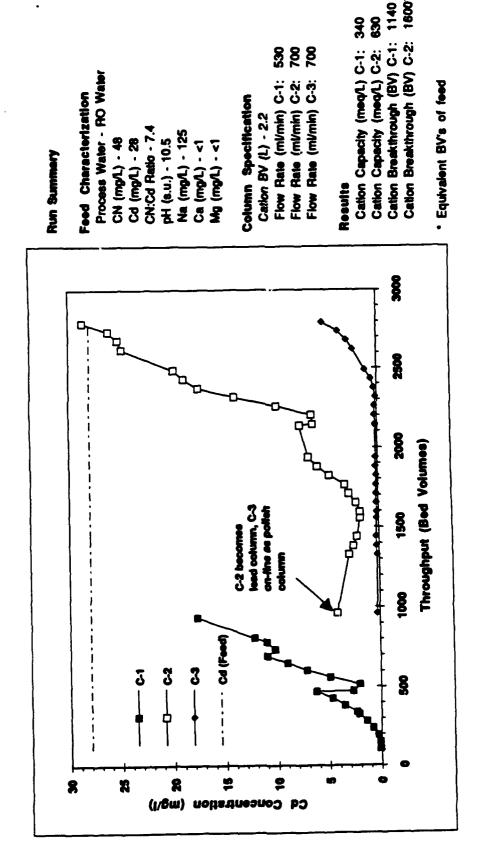


B-6

Source: Arthur D. Little, Inc.

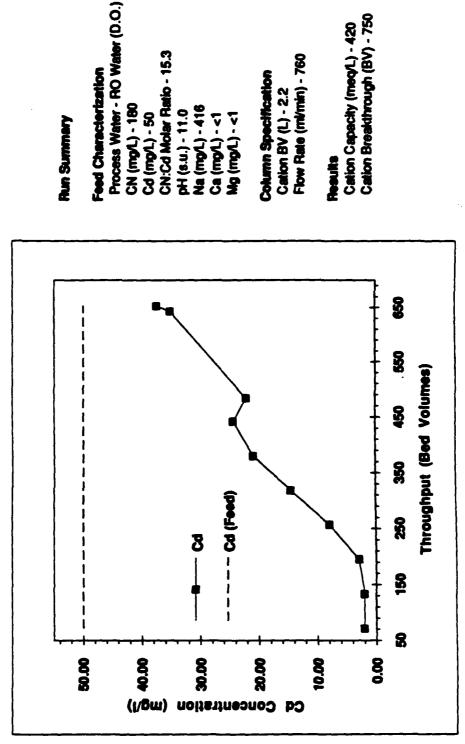
. .

Figure B-5: Columns C-1, C-2, and C-3 Breakthroughs (Runs BC-8, BC-9, and BC-10) 6/15-6/23



Source: Arthur D. Little, Inc.

Figure B-6: Column C-1 Breakthrough (Run BC-11) 6/24-6/25



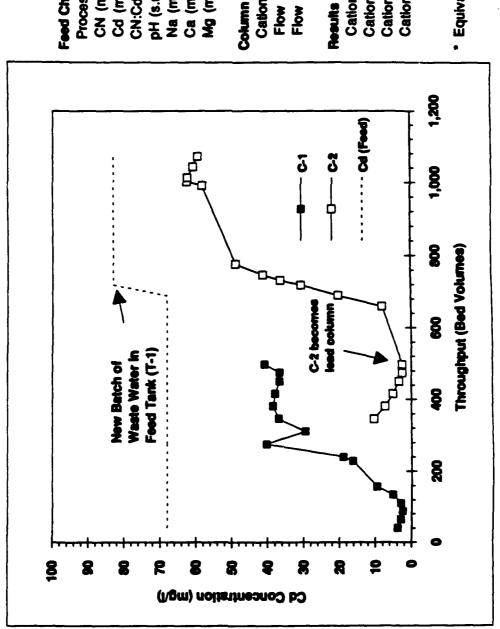
Run Summery

CN:Cd Molar Ratio - 15.3 CN (mg/L) - 180 Na (mg/L) - 416 PH (s.u.) - 11.0 Cd (mg/L) - 50 Ca (mg/L) - <1 Mg (mg/L) - <1

Flow Rate (mi/min) - 760 Column Specification **Cation BV (L) - 2.2** 

Cation Breakthrough (BV) - 750 Cation Capacity (meq/L) - 420 **Peaults** 

Figure B-7: Columns C-1 and C-2 Breakthroughs (Runs BC-12 and BC-13) 7/20-7/22



CN (mg/L)-81 (Run BC-12), 79 (Run BC-13) Cd (mg/L)-68 (Run BC-12), 83 (Run BC-13) Process Water - CdCN Rinse (CW High Cd) CN:Cd Molar Ratio - 5.1, 4.1 Feed Characterization Na (mg/L) - 317 Ca (mg/L) - 12 Mg (mg/L) - 23 pH (s.u.) - 9.8

Cation BV (L) - 2.2 Column Specification

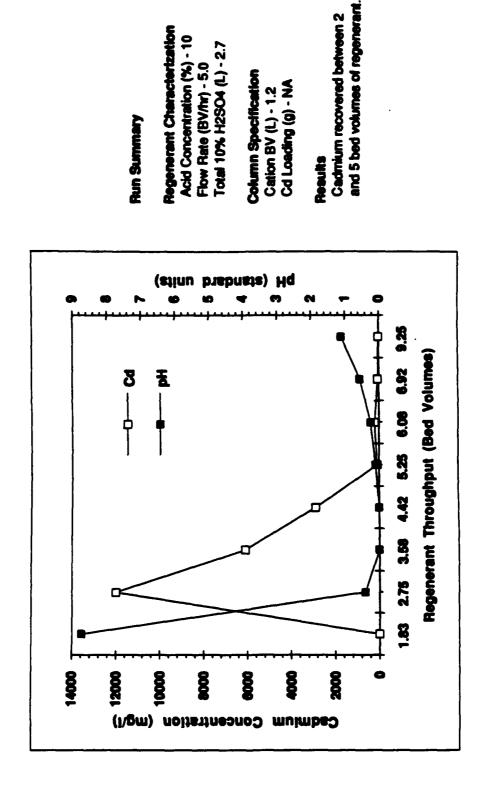
Flow Rate (ml/min) C-2: 550 Flow Rate (ml/min) C-1: 430

Cation Capacity (meq/L) C-2: 520 Cation Capacity (meq/L) C-1: 330 Cation Breakthrough (BV) C-1: Breakthrough (BV) C-2: Cation

• Equivalent BV's of feed

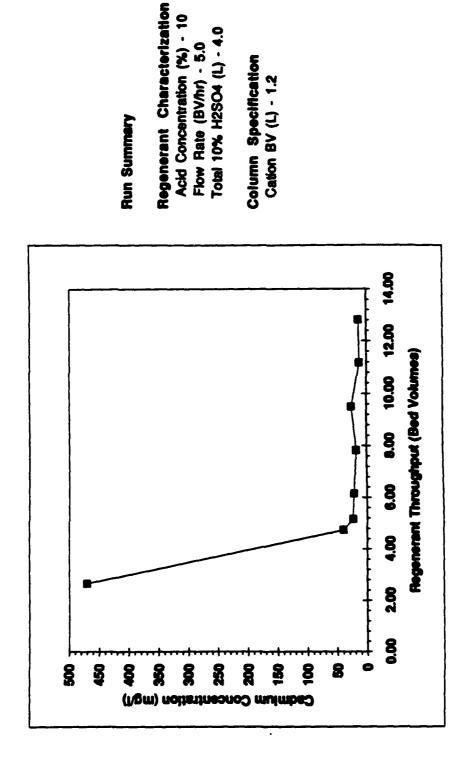
Source: Arthur D. Little, Inc.

Figure B-8: Column C-1 Regeneration (Run RC-3) 4/16



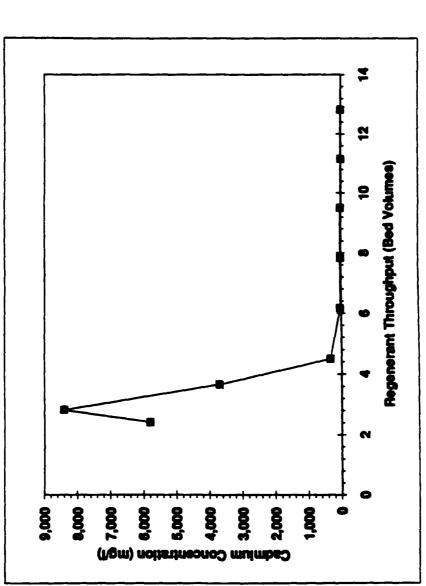
Source: Arthur D. Little, Inc.

Figure B-9: Column C-2 Regeneration (Run RC-4) 4/16



Source: Arthur D. Little, Inc.

Figure B-10: Column C-3 Regeneration (Run RC-5) 4/16



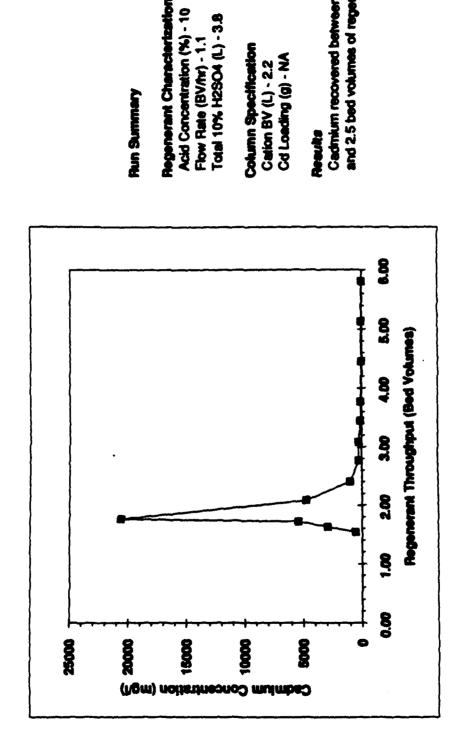
**Run Summary** 

Regenerant Characterization Acid Concentration (%) - 10 Flow Rate (BV/hr) - 4.0 Total 10% H2SO4 (L) - 2.4

Column Specification Cation BV (L) - 1.2 Cd Loeding (g) - NA Results
Cadmium recovered between 1.5
and 5 bed volumes of
throughput.

Source: Arthur D. Little, Inc.

Figure B-11: Column C-1 Regeneration (Run RC-6) 5/15

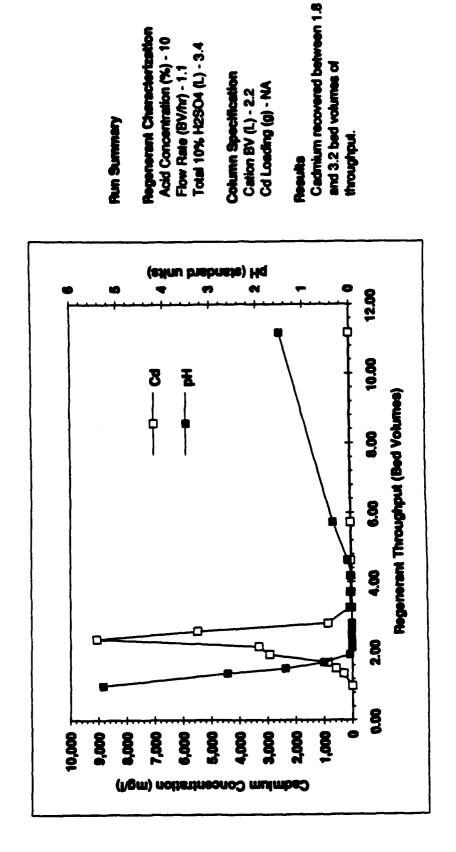


Acid Concentration (%) - 10 Flow Rate (BV/hr) - 1.1 Total 10% H2SO4 (L) - 3.8

and 2.5 bed volumes of regenerant. Cadmium recovered between 1.5

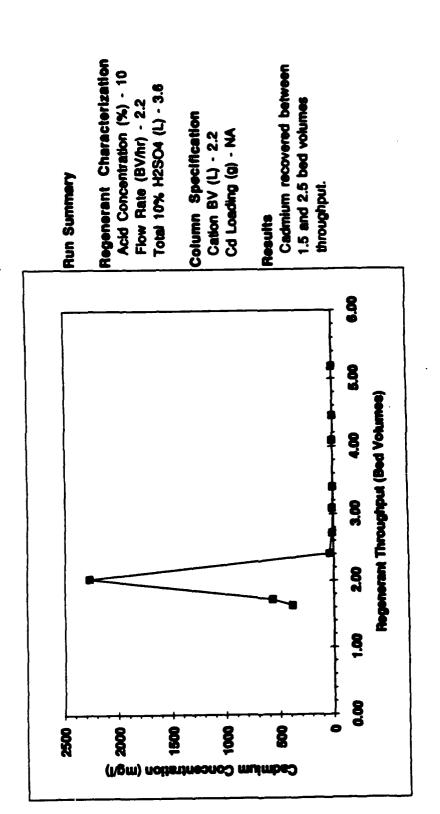
Cd Loading (g) - NA

Figure B-12: Column C-3 Regeneration (Run RC-7) 5/14



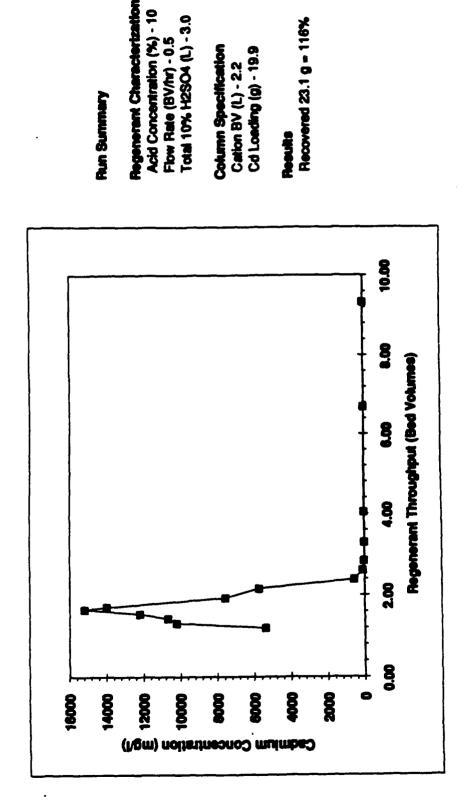
Source: Arthur D. Little, Inc.

Figure B-13: Column C-2 Regeneration (Run RC-8) 5/16



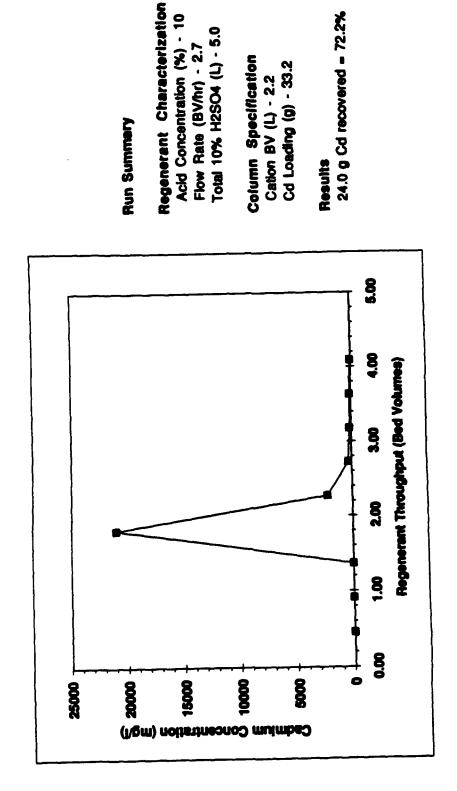
Source: Arthur D. Little, Inc.

Figure B-14: Column C-1 Regeneration (Run RC-9) 6/11



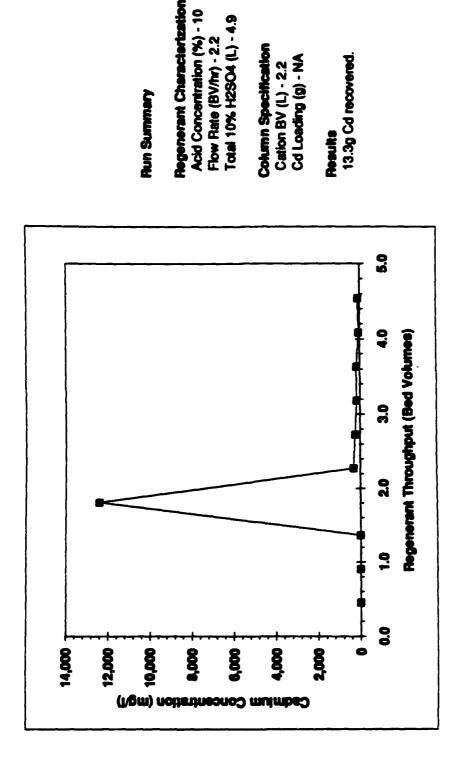
Source: Arthur D. Little, Inc.

Figure B-15: Column C-2 Regeneration (Run RC-10) 6/12



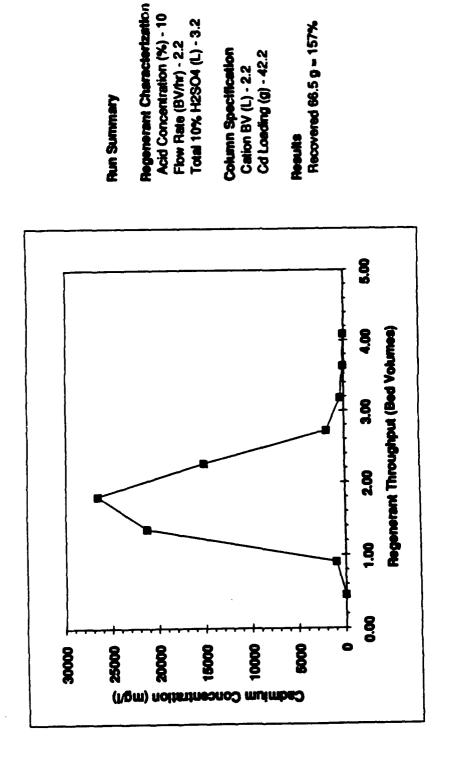
Source: Arthur D. Little, Inc.

Figure B-16: Column C-3 Regeneration (Run RC-11) 6/15



Source: Arthur D. Little, Inc.

Figure B-17: Column C-1 Regeneration (Run RC-12) 6/20



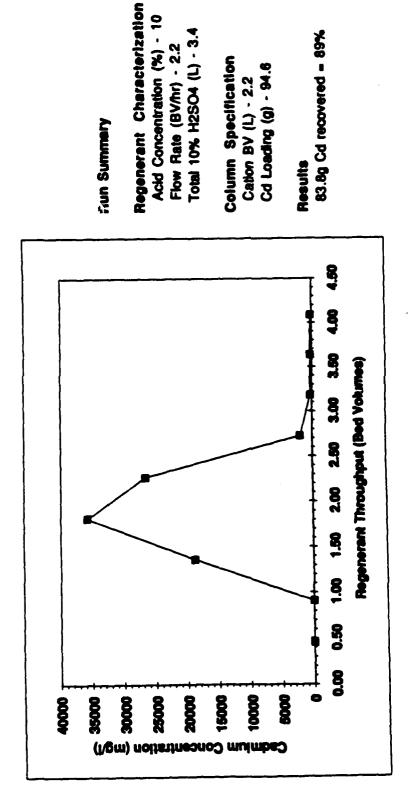
Acid Concentration (%) - 10

Recovered 66.5 g = 157%

Cd Loading (g) - 42.2

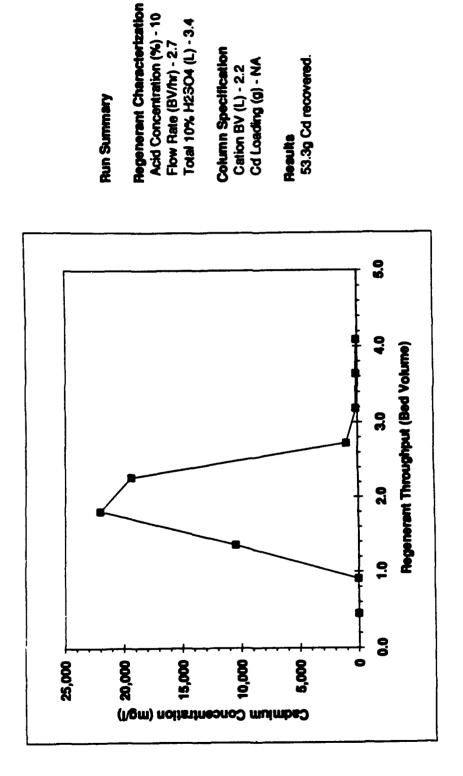
Source: Arthur D. Little, Inc.

Figure B-18: Column C-2 Regeneration (Run RC-13) 6/24



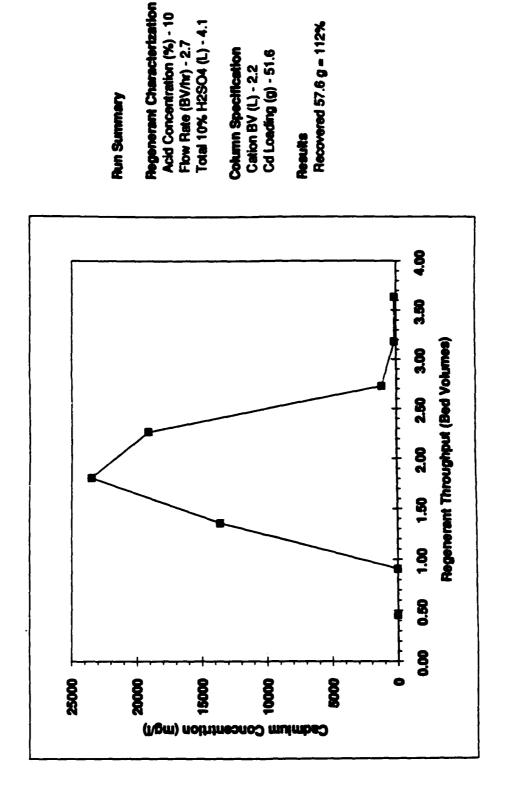
Source: Arthur D. Little, Inc.

Figure B-19: Column C-3 Regeneration (Run RC-14) 6/24



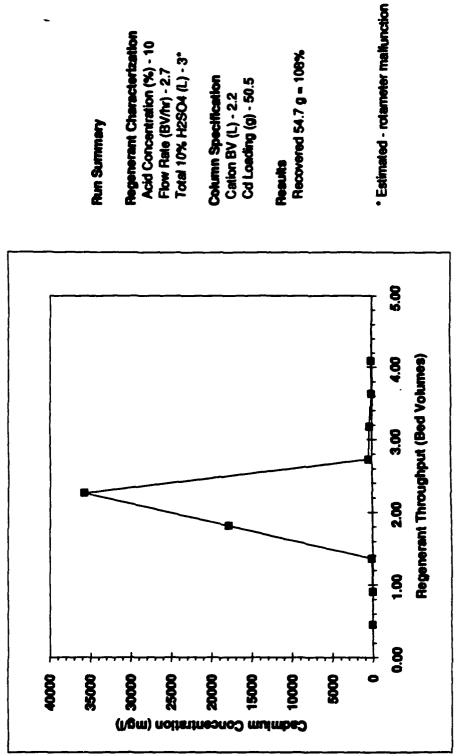
Source: Arthur D. Little, Inc.

Figure B-20: Column C-1 Regeneration (Run RC-15) 6/25



Source: Arthur D. Little, Inc.

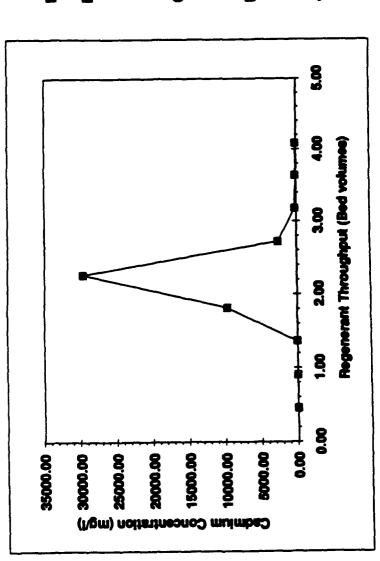
Figure B-21: Column C-1 Regeneration (Run RC-16) 7/22



Cd Loading (g) - 50.5

Acid Concentration (%) - 10 Flow Rate (BV/hr) - 2.7 Total 10% H2SO4 (L) - 3\*

Figure B-22: Column C-2 Regeneration (Run RC-17) 7/23



Run Summary

Regenerant Characterization Acid Concentration (%) - 10 Flow Rate (BV/hr) - 2.7 Total 10% H2SO4 (L) - 3\*

Column Specification
Catton BV (L) - 2.2
Cd Loading (g) - 62.9
Results

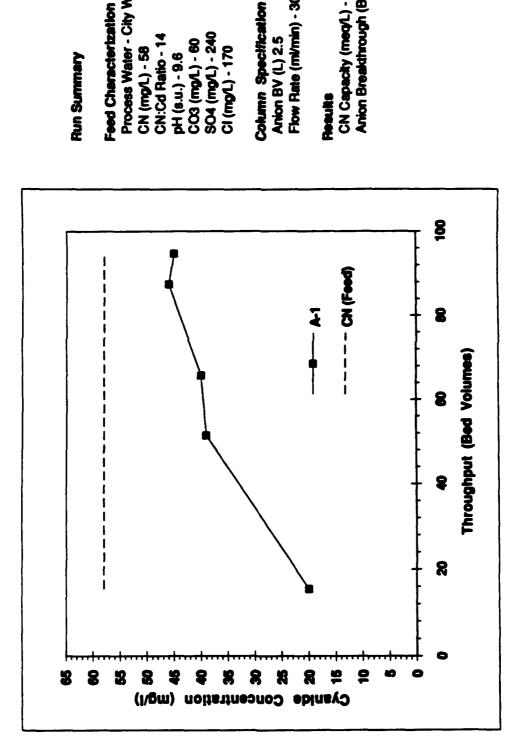
42.2g Cd recovered = 67%

· Estimated - rotameter malfunction

Source: Arthur D. Little, Inc.

Appendix C: Anion Column Breakthrough and Regeneration Curves

Figure C-1: Col. An A-1 Breakthrough (Run BA-2) 4/13-4/14



Process Water - City Water

Anion Breakthrough (BV) - 87

CN Capacity (meq/L) - 90

Flow Rate (m/rmin) - 300

Anion BV (L) 2.5

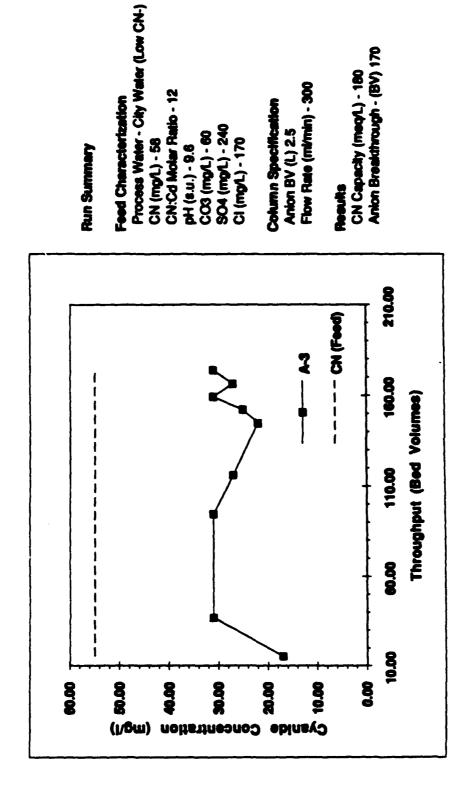
SO4 (mg/L) - 240

CI (mg/L) - 170

CO3 (mg/L) - 60

pH (s.u.) - 9.6

Figure C-2: Column A-3 Breakthrough (Run BA-3) 4/14-4/15



Source: Arthur D. Little, Inc.

Figure C-3: Column A-1 Breakthrough (Run BA-4) 6/15-6/16

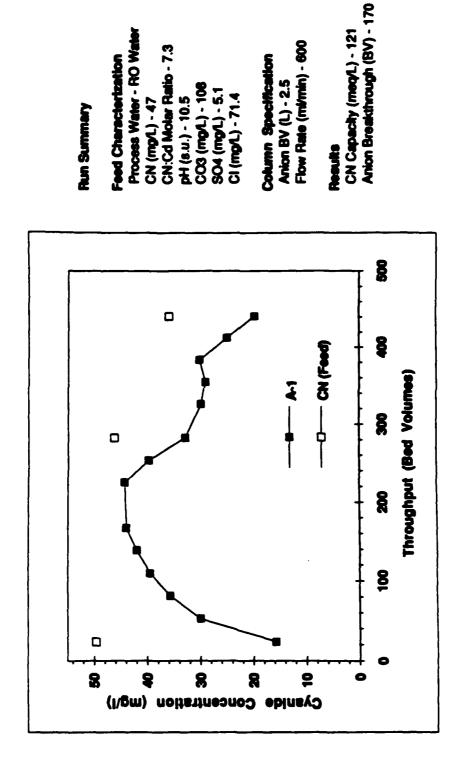


Figure C-4: Column A-1 Breakthrough (Run BA-5) 6/20

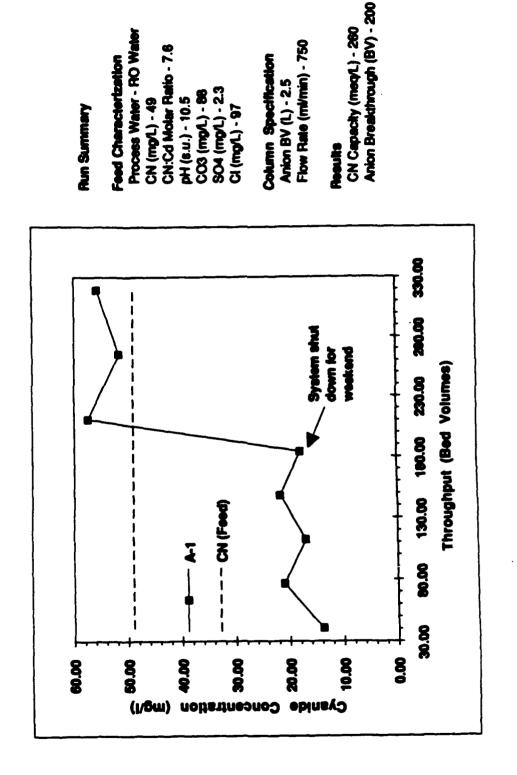
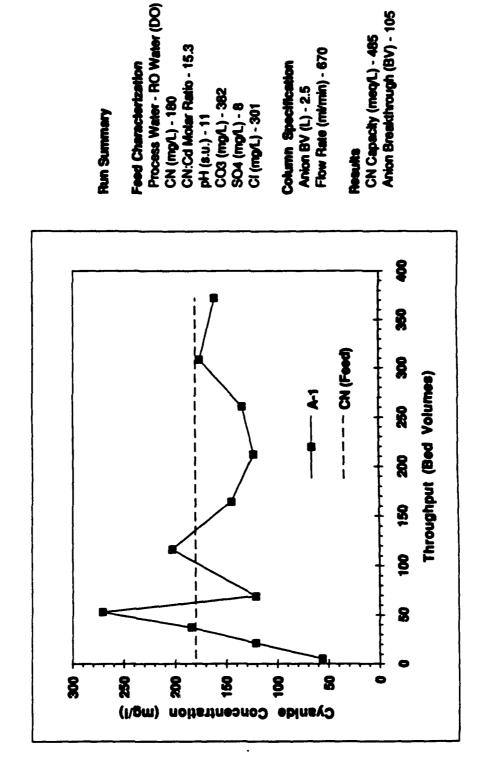
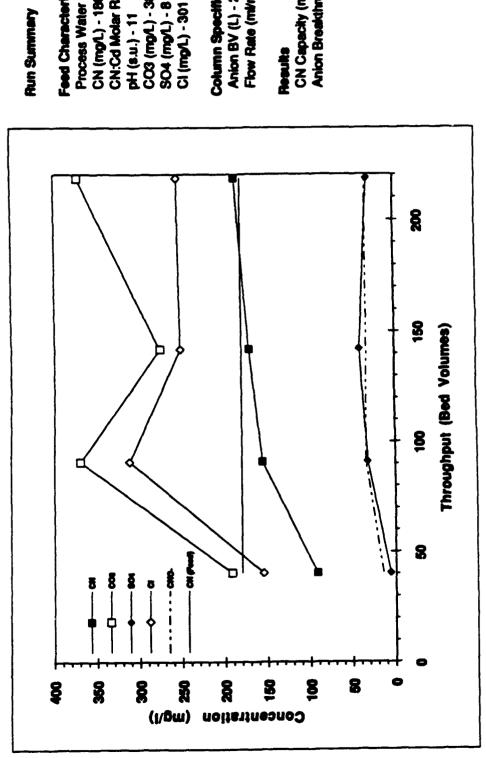


Figure C-5: Column A-1 Breakthrough (Run BA-6) 6/24



Source: Arthur D. Little, Inc.

Figure C-6: Column A-2 Breakthrough (BA-7) 6/25



Run Summery

Process Water - RO Water (DO) CN (mg/L) - 180 CN:Cd Molar Ratio - 15.3 Feed Characterization pH (s.u.) - 11 CO3 (mg/L) - 382 SO4 (mg/L) - 8

Flow Rate (mi/min) - 1060 Column Specification Anion BV (L) - 2.5

Anion Breakthrough (BV) - 180 CN Capacity (meq/L) - 410 Postults

Figure C-7: Column A-1 Regeneration (Run RA-1) 4/13

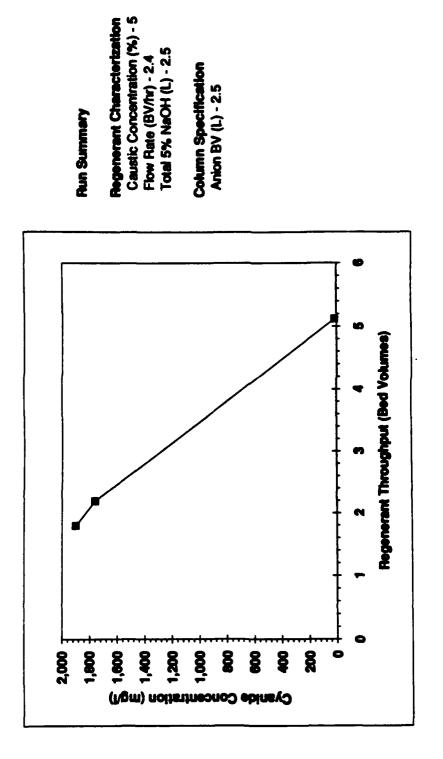
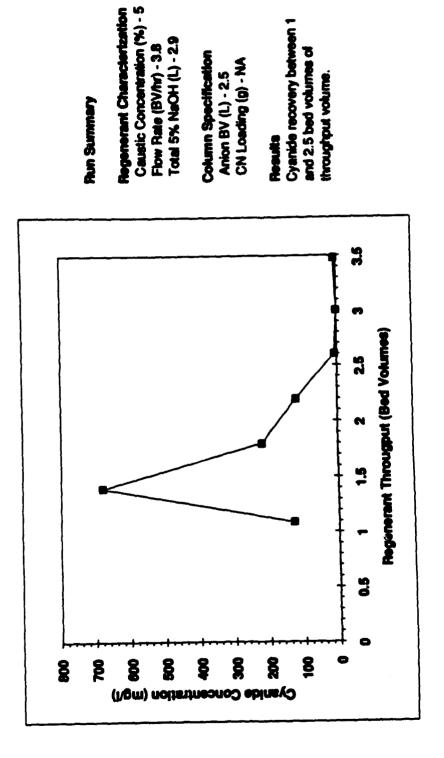
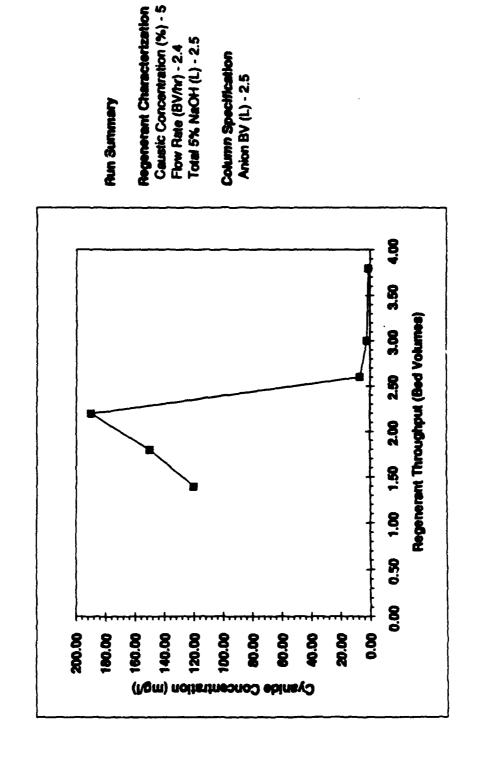


Figure C-8: Column A-2 Regeneration (Run RA-4) 4/15



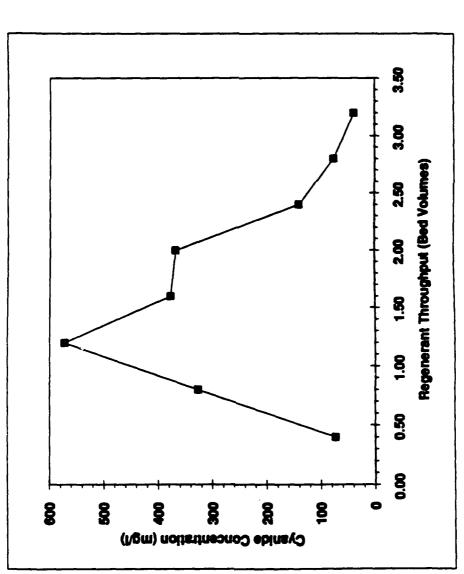
Source: Arthur D. Little, Inc.

Figure C-9: Column A-3 Regeneration (Run RA-5) 4/16



Source: Arthur D. Little, Inc.

Figure C-10: Column A-1 Regeneration (Run RA-6) 6/18

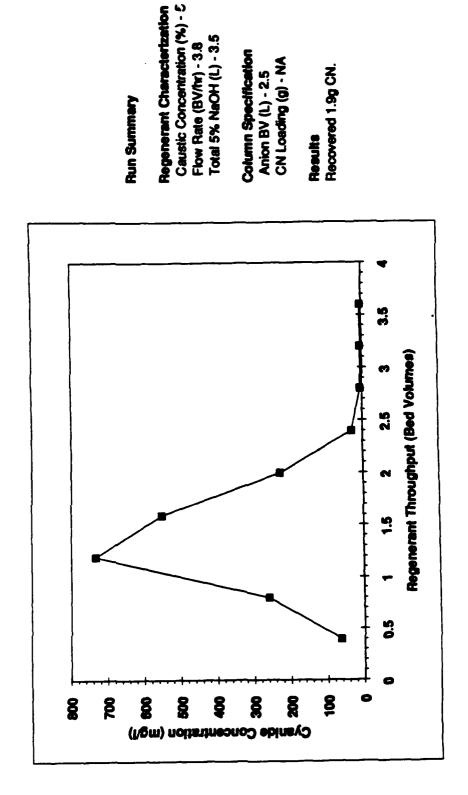


Regenerant Characterization Caustic Concentration (%) - 5 Flow Rate (BV/hr) - 3.8 Total 5% NaOH (L) - 3.7 Column Specification Anion BV (L) - 2.5 CN Loading (g) - 18.2

Run Summary

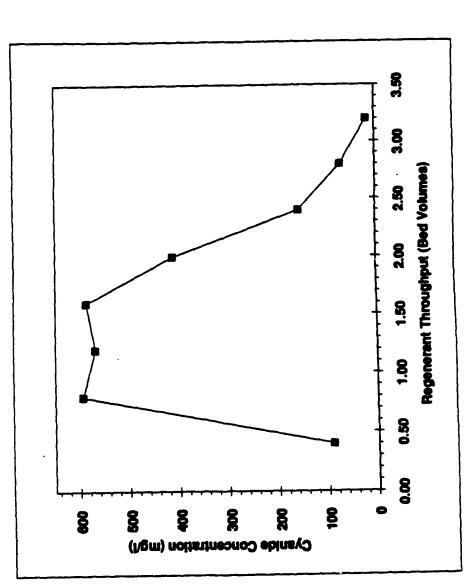
Recovered 2.1 g = 12%

Figure C-11: Column A-2 Regeneration (Run RA-7) 6/18



Source: Arthur D. Little, Inc.

Figure C-12: Column A-1 Regeneration (Run RA-8) 6/23



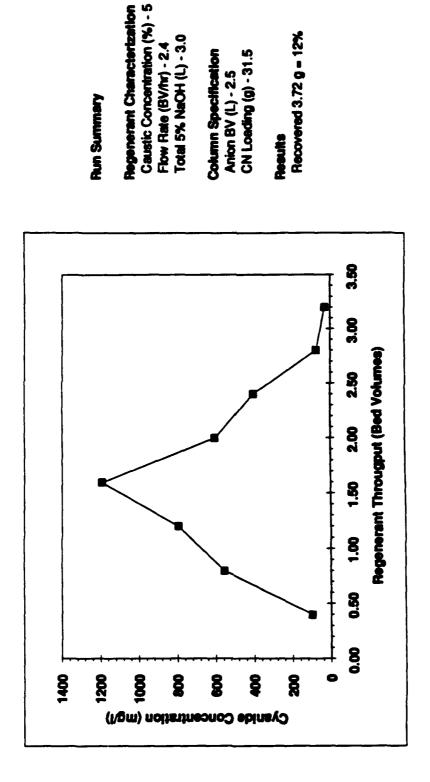
Run Summary

Regenerant Characterization Caustic Concentration (%) - 5 Flow Rate (BV/fr) - 2.4 Total 5% NaOH (L) - 3.2

Column Specification Anion BV (L) - 2.5 CN Loading (g) - 16.7 Recovered 2.5 g = 15%

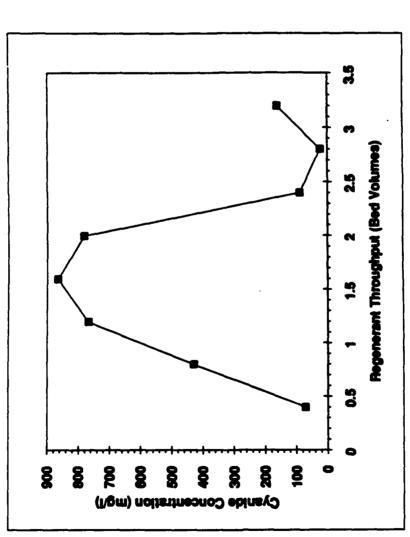
Source: Arthur D. Little, Inc.

Figure C-13: Column A-1 Regeneration (Run RA-9) 6/25



Source: Arthur D. Little, Inc.

Figure C-14: Column A-2 Regeneration (Run RA-10) 6/26



Caustic Concentration (%) - 5 Regenerant Characterization

**Run Summery** 

Total 5% NaOH (L) - 3.0 Flow Rate (BV/hr) - 2.4

CN Loading (g) - 26.6

Recovered 3.2g = 12%

Results

Column Specification

Anion BV (L) - 2.5

## Appendix D: Summary of Analytical Results

NCEL Ion Exchange Pilot Program Sample Results (mg/l)

ф В		2.9			0.15										2.1																			
0					Ö																													
æ		0.29			2										0.30																			
2		24			26										28																			
8		42			82				4200	1700	430				34																			
ច		170			10										160																			
8		240			250				1700	9100					250																			
<b>5</b> 0																																		
8		90			12					2				2900	38																			
£		220			110										190																			
Cd (Tot) Cd (Diss)				2	2	0.15			0.60	2500	<b>→</b>				17	17.8						4.63	4.08	6.21	7.3	2								22
ક	55			0.05			12	62				1900		13	47	91.2	10.6	38.7	40.3	45.7	44.7					64.3	130	680	220	120	7.1	0.54	<b>4</b> .	9
SAMPLING DATE	04/08/92	04/08/92	04/08/92	04/08/92	04/08/92	04/09/92	04/09/92	04/09/92	04/10/92	04/10/92	04/10/92	04/11/92	04/11/92	04/11/92	04/13/92	04/13/92	04/13/92	04/14/92	04/14/92	04/14/92	04/14/92	04/13/92	04/14/92	04/14/92	04/14/92	04/14/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92
SAMPLE	12:30	12:30	12:30	04:00	13:00	10:25	15:00	23:00	03:10	03:22	03:45	02:10	02:50	03:15	00:60	18:00	20:09	01:09	03:00	60:80	60:60	22:42	03:42	08:42	10:42	11:00	08:42	08:55	00:00	90:00	09:10	09:15	06:30	08:00
SAMPLE LOCATION	7	T-1 (2)	1:1	Final Eff	Tap Water	C-1 1-9 S1	A-1 2-2 S2	A-1 2-10 S2	C-1 Regen	C-1 Regen	C-1 Regen	A-1 Regen	A-1 Regen	A-1 Rinse 2	Rinse Tank	1.1	A-1 Eff	A-1 E#	A-1 Eff	A-1 E#	A-1 E#	C-1 Eff	C-1 E#	C-1 E#	C-1 Process	Final Eff	A-2 Regen	A-2 S Films	A-2 S Rinse	A-2 S Rinse	A-2 S Rinse	A-2 F Rinse	A-2 F Rinse	1:1
SAMPLE	100	101	102	103	104	105	106	107	108	100	110	111	112	113	114	115	116	117	118	119	120	121	122	123	136	124	125	126	127	128	129	130	131	132

NCEL Ion Exchange Pilot Program Sample Results (mg/l)

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2																												3007		249		<u>.</u>	!	<b>58</b> .3	
8																												<b>2</b> 03		791		874	,	900	
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2																												168		101		95.6		92.2	
Cd (Tot) Cd (Diss)																													•						
e Po	12	12	12	=						2	11.8	11.2	10.3														18.6	1.60	11845	6092	2937	92.3	195	46.3	32.7
8					17	78	31	27	28					21.8	25.4	30.9	27.4	30.7	45.3	184	124	150	188	6.9	2.7	<b>8</b> .	36.7								
SAMPLING DATE	04/14/92	04/14/92	04/15/92	04/15/92	04/14/92	04/14/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/15/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92
SAMPLE	17:42	21:42	01:42	05:42	15:09	18:09	03:00	60:90	11:10	12:10	09:42	12:42	15:42	11:09	12:09	13:09	14:09	15:09	14:40	16:50	17:35	17:40	17:46	17:50	17:55	18:05	00:00	00:40	10:05	10:10	10:15	10:20	10:25	10:30	10:45
SAMPLE LOCATION	C-1 Process	C-1 Process	C-1 Process	C-1 Process	A-3 Process	A-3 Process	A-3 Process	A-3 Process	Final Eff	Final EN	C-1 Process	C-1 Process	C-1 Process	A-3 Process	C-2 Process	A-3 Regen	A-3 S Rinse	A-3 S Pinee	A-3 S Rinse	A-3 S Rinse	A-3 S Rinse	A-3 S Rinse	· T:	C-1 Regen	C-1 S Pine	C-1 S Rinse	C-1 S Filme	C-1 8 Rinse	C-1 S Fine	C-1 S Plines	C-1 F Rinse				
SAMPLE	134	135	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	<b>9</b> D-4

NCEL Ion Exchange Pilot Program Sample Results (mg/l)

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į	2									56.5		<b>58.6</b>		14.8		9.52		3518		236		26.1		9.0		<u> </u>						•	21.0				
é	5									743		754		641		700		958		704	;	60		307	,	387						•	4.0				
į	3																																162.2				
į	Ž																															•	187				
Î	2																																				
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;	<b>2</b>									20		83.8		72.8		80.5		87.8		<b>2</b>		1612		786		1697											
	Cd (Tot) Cd (Diss)	0.02	0.03	0.43	0.52	2.26	2.61	3.68	4.57	474	38.6	24.2	21.5	16.6	25.3	12,3	12.7	2008		3698		33.2	18.6	13.9	8.18	10.6							22.4	1.02		3.52	
	3	42.2	4.14	34.9	26.6	30.1	34.0																									85.0			74.6		
SAMPLING	DATE	04/16/92	04/15/92	04/15/92	04/15/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92	04/16/92						05/13/92	05/13/92	05/12/92	05/12/92	05/12/92	
SAMPLE	IME	17:42	19:42	21:42	11:42	01:42	03:42	05:42	07:42	14:55	15:10	15:15	15:25	15:30	15:35	15:40	15:45	16:45	16:50	17:00	17:10	17:25	17:30	17:35	17:40	17:45						00:00	00:00	00:60	00:60	11:00	
SAMPLE	LOCATION	C-3	C-3	ر. د:3	C-3	C-3	C-3	C-3	C-3	C-2 Regen	C-2 Regen	C-2 Regen	C-2 Regen	C-2 Regen	C-2 Regen	C-2 Regen	C-2 Regen	C-3 Regen	,					<u>:</u>	-	<u>c</u> .	<u>.</u>	<b>c</b> .1									
SAMPLE		170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	180	191	192	103	194	195	196	197	198	199	200	201	202	203	204	-5

NCEL Ion Exchange Pilot Program Sample Results (mg/l)

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Cd (Tot) Cd (Diss)		0.25	0.32	0.21		0.19	0.92	0.2	0.16		0.15	0.19	0.5		1.15		1.45		2.84		18.3		2.26	0.11		0.16	<b>o</b> .	80.0		0.07	0.07	90.0		,	21.0	
3					59.1					53.8				52		52.7		62.2		62.8		77.1			75.1				<b>9.99</b>				78.9			62.5
SAMPLING DATE		05/12/92	05/12/92	05/12/92	05/12/92	05/12/92	05/12/92	05/12/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/12/92	05/12/92	05/12/92	05/12/92	05/12/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92	05/13/92
SAMPLE		13:00	15:00	17:00	17:00	19:00	21:00	23:00	01:00	01:00	03:00	00:90	00:90	00:90	08:30	08:30	10:00	10:00	11:30	11:30	10:00	10:00	08:40	12:40	12:40	16:40	20:40	00:40	00:40	02:40	04:40	06:40	06:40		08:40	08:40
SAMPLE		:	:	<u>:</u>	<u>-</u> -	. <del>.</del>	:	<del>.</del> 5	5-	<u>:</u>	C-1	<u>:</u>	<u>ن</u>	:	<u>:</u>	5-1	<b>C-1</b>	<u>:</u>	<del>1.</del> 5	<u>6.</u>	<u>-</u>	<u>:</u>	G-3	C-3	C-3	C-3	င်းဒ	6:3	C-3	C-3	6.3	C-3	C-3	8	1:1	1:1
SAMPLE .		202	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237		<b>5</b> 5-6

05/13/92 46.7 0.06 05/13/92 46.7 0.05 05/13/92 63.9 0.14 05/13/92 45.9 0.14 05/13/92 45.9 0.04 05/13/92 41.1 0.02 05/13/92 41.1 0.02 05/13/92 54.2 0.03 05/13/92 54.2 0.03 05/13/92 54.1 0.04 05/13/92 54.2 0.03 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04 05/13/92 54.1 0.04
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6. 6. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4.
6. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4.
6. 1. 5. 2. 2. 4. 6. 6. 6. 6. 6. 6. 6. 6. 6. 6. 6. 6. 6.
6. 1. 5. 1. 6. 6. 6. 6. 6. 6. 6. 6. 6. 6. 6. 6. 6.
1. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4.
1.1 4.2 4.2 4.4 4.4 4.4 4.4 4.4 4.4 4.4 4.4
2. 2. 2
2. <del>1.</del> 5.
2. 4. 5. 5. 5. 5. 5. 5. 5. 5. 5. 5. 5. 5. 5.
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<b>-</b>
05/14/92 303 05/14/92 585 05/14/92 2930 05/14/92 2930 05/14/92 9060 05/14/92 5480 05/14/92 66.6 05/14/92 66.6 05/14/92 66.6
05/14/92 5.37
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NCEL Ion Exchange Pilot Program Sample Results (mg/l)

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8																										2.23									
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8																										78.1									
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8																										247									
<b>8</b> E																																			
8																									•	30.5									
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Cd (Tot) Cd (Diss)	0	00	0	0	9	•	6	7	၈	œ	8		•	•	0	-	<b>6</b> 0	-	7	so.	-	10				29.4	•	8		7	•	•	7	<b>6</b>	
3	5440	20600	4790	1010	. 25	260	103	84.7	62.3	42.	<del>1</del> 5.		36	28	227	40	12.8	6.61	5.7	2.45	1.71	0.2				29.9	0.0	28.2	8	0.5	7.0	<u> </u>	2.67	4.5	<b>1</b> 0
8																										<b>9.99</b>		41.2	42						
SAMPLING DATE	05/16/92	05/15/92	05/15/92	05/15/92	05/15/92	05/15/92	05/15/92	05/15/92	05/15/92	05/15/92	05/15/92	05/15/92	05/16/92	05/16/92	05/16/92	05/16/92	05/16/92	05/16/92	05/16/92	05/16/92	05/16/92	05/16/92	05/16/92	05/16/92	05/16/92	06/08/92	06/09/92	06/09/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92
SAMPLE	09:50	09:45	09:50	99:58	10:00	10:05	10:10	10:15	10:25	10:35	10:45	••	15:15	15:20	15:25	15:30	15:35	15:40	15:45	15:55	16:00	16:10	••	••	••	16:00	07:30	07:30	07:20	08:15	10:15	12:15	14:15	16:15	18:15
SAMPLE	C-1 Regen		တ	C-1 S Rinse		C-1 S Rinse		C-2 Regen	C-2 S Rinse	C-2 S Rinse		C-2 S Rinse	C-2 S Rinse			C-2 S Rinse	C-2 F Rinse				<u>:</u>	<del>ن</del> -	7:1	1:1	<u>.</u>	C-1	<u>:</u>	C-3	<u>c-1</u>	<u>:</u>					
SAMPLE	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	308	306	307	308	<b>6</b> 00 D-1

NCEL Ion Exchange Pilot Program Sample Results (mg/l)

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<b>5</b>																																				
8																	27.4																			
Z																	207																			
Cd (Tot) Cd (Dies)		6.7	19.7	9.6	50.6	6.6	20.4	20.2	2	8.8	19.3	16.4	9.9	16.7		28.4 27.1	28.4	380	10200	0020	2200	15200	14000	1570	2750	<b>56</b> 5	11	<b>46.6</b>	29.4	35.6	12	6.40	0.02	0.12	0.03	
8		•	•	•	•			••								<del>-</del> .			_	-	-	_	<b>,</b>													
0																•••																				
SAMPLING	76/01/00	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/10/92	06/11/92	06/11/92	06/11/92	06/11/92	08/11/92	06/11/92	06/11/92	06/11/92	06/11/92	06/11/92	06/11/92	06/11/92	06/11/92	06/11/92	06/11/92	06/11/92	06/11/92	06/11/92	06/11/92	
SAMPLE	61.03	22:15	00:15	02:15	04:15	06:15	07:15	08:30	11:00	09:15	11:15	13:15	15:15	15:30	15:30	17:00	07:30	09:15	09:25	09:35	09:45	09:55	10:00	10:10	10:15	10:20	10:25	10:30	10:40	10:55	11:05	11:15	16:40	18:40	20:40	
SAMPLE	<u>.</u>	<del>.</del>	. <del>.</del>	<u>ن</u>	<del>د.</del> 1	<del>ن</del>	<u>c.</u>	<u>:</u>	C-2	c.1	c-1	د-1	c.1	c.1	C-5	1.1	1:1	C-1 Regen					C-1 Regen	Ø	C-1 S Rinse	C-1 F Rinse	C-1 F Rinse	C-1 F Rinse	C-2	C-2	C-5					
SAMPLE	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	338	340	341	342	343		-9

NCEL ion Exchange Pilot Program Sample Results (mg/l)

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(Diss																															
Cd (Tot) Cd (Diss)	0.02	0.02	0.03	0.05	0.02 0.05	0.43	1.49	2.39	2070	29.7	878	507	£79	386	7.55	1.0	12	12.5	13.6	14.4	14.7	<u>s</u>	14.7	4.4.4	9.65	1.03	1.04	•	21000	2200	299
CN Cd (Tot) Cd	0.05	0.05	0.03	0.02	0.02 0.05	0.43	1.49	2.39		35.7 29.7	878	507	6/9	386	7.55	9.1	12	12.5	13.6	14.4	14.7	<b>S</b>	14.7	4.4	9.65	1.03	1.94	••	21000	2200	500
	06/11/92 0.02	06/11/92 0.02			06/11/92					35.7				06/12/92 386	06/11/92 7.55		06/11/92 12								06/12/92						06/12/92 299
3	<b>≈</b>	06/11/92	06/11/92	06/11/92		06/11/92	06/11/92	06/11/92	06/12/92	06/12/92 35.7	06/12/92	06/12/92	06/12/92		06/11/92		06/11/92	06/11/92	06/12/92	06/12/92	06/12/92	06/12/92	06/12/92	06/12/92		06/12/92	06/12/92	06/12/92	06/12/92	06/12/92	06/12/92
SAMPLING DATE ON	06/11/92	00:40 06/11/92	02:40 06/11/92	04:40 06/11/92	06/11/92	10:40 06/11/92	12:40 06/11/92	14:40 06/11/92	07:50 06/12/92	06/12/92 35.7	09:50 06/12/92	11:30 06/12/92	15:00 06/12/92	06/12/92	17:40 06/11/92	19:40 06/11/92	21:40 06/11/92	23:40 06/11/92	01:40 06/12/92	03:40 06/12/92	06/12/92	06:40 06/12/92	06:40 06/12/92	10:40 06/12/92	06/12/02	Regen 16:25 06/12/92	16:40 06/12/92	16:53 06/12/92	17:07 06/12/92	17:34 06/12/92	17:39 06/12/92

NCEL Ion Exchange Pilot Program Sample Results (mg/l)

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8																					2															
5																					71.4															
8																					-															
2																																408	368			
8																					108.2															
2																					128															
Cd (Tot) Cd (Diss)	109	86	0.5	80.0	0.04	0.03	0.03	0.04	0.12	0.33	0.61	1.31	1.44	1.79	1.41	<b>*</b> :-	2.4	2.83	2.59	3.45	24.1	0.03	0.07	3.93	12400	328	238	164	164	49.5	92.7	2	27.8	6.3	0.34	
8																					49.7											4.35	46.3			
SAMPLING DATE	06/12/92	06/12/92	06/11/92	06/11/92	06/11/92	06/11/92	06/12/92	06/12/92	06/12/92	06/12/92	06/12/92	06/12/92	06/12/92	06/12/92	06/12/92	06/12/92	06/12/92	06/12/92	06/13/92	06/13/92	06/13/92	06/15/92	06/15/92	06/15/92	06/15/92	06/15/92	06/15/92	06/15/92	06/15/92	06/15/92	06/16/92	06/16/92	06/16/92	06/16/92	06/16/92	
SAMPLE	17:50	17:55	16:15	19:15	20:15	22:15	00:15	02:15	04:15	06:15	08:15	10:15	12:15	14:15	16:15	19:00	20:00	20:30	07:00	00:60		09:57	10:13	10:29	10:45	11:05	11:15	11:25	11:33	11:42	11:58	15:00	07:30	11:30	14:30	
SAMPLE	C-2 Regen	C-2 Regen	c.3	C-3	C-3	C-3	C-3	C-3	1:1	C-3	C-3	C-3	C-3 S Rinse	C-3 S Pinse	C-3 S Pines	C-3 S Rinse	C-3 S Pinse	C-3 S Rinse	C-3 F Rinse	Final Eff.	T-1	C-1	<del>د</del> .													
SAMPLE	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	D-	- ]

NCEL Ion Exchange Pilot Program Sample Results (mg/l)

SAMPLE	SAMPLE	SAMPLE	SAMPLING												
NUMBER	LOCATION	TIME	DATE	8	Cd (Tot) Cd (Diss)	2	8	2	Š	อ	8	\$	£	8	Ś
415	<b>C-1</b>	17:30	06/16/92		0.13										
416	<u>-</u> -	20:30	06/16/92		0.14										
417	<u>.</u>	23:30	06/16/92		0.3										
418	:	02:30	06/16/92		0.81										
419	<del>د</del> .	02:30	06/16/92		1.43										
420	5-1	08:30	06/16/92		2.15										
421	8	07:30	06/16/92	102	2650										
422	2	06:60	06/16/92		2000										
423	æ	11:30	06/16/92		1890										
424	Œ	16:30	06/16/92		1560										
425	A-1	11:40	06/15/92	15.8											
426	A-1	13:40	06/15/92	30											
427	A-1	15:40	06/15/92	35.7											
428	A-1	17:40	06/15/92	39.5											
429	A-1	19:40	06/15/92	42.1											
430	A-1	21:40	06/15/92	7											
431	A-1	11:40	06/15/92	61.8											
432	A-1	13:40	06/15/92	44.3											
433	A-1	15:40	06/15/92	39.8											
434	A-1	17:40	06/15/92	32.9											
435	A-1	19:40	06/15/92	21.7											
436	A-1	20:40	06/15/92	29.9											
437	Final Eff	22:15	06/16/92	28.6	0.02			369							
438	-	17:25	06/16/92	36	30.4										
430	Final Eff	18:30	06/16/92	31.5	2										
440	A-1	10:40	06/16/92	29.1											
441	A-1	12:40	06/16/92	30.2											
442	A-1	14:40	06/16/92	<b>5</b> 2											
443	A-1	16:40	06/16/92	<b>10.8</b>											
777	A-1	18:30	06/16/92	42.1											
445	:	08:30	06/16/92		2.36										
446	ပ်	12:30	06/16/92		3.52										
447	c. 1-3	15:30	08/18/92		4.72										
448	<u>:</u>	18:30	06/16/92		6.26										
D-	1.1	00:60	06/11/95	54.4	29.3	128	102		3.5	109.6	2	2	0.36	2	
-12															

Š		2.01																																	
8																																			
æ																																			
\$																																			
8																																			
ច																																			
8																																			
2																																			
8																																			
2																																			
Cd (Tot) Cd (Diss)	2	30.5	994	809	808	495	495	2.7	2.05	4.9	7.17	9.05	11	10.2	=	12.2										0.0									•
8	46.2	60.9															73.5	327	573	377	368	140	78.1	38.8	22.4		62.8	261	733	<b>6</b> 82	228	30.9	5.24	4.5	4.03
SAMPLING DATE	06/17/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/17/92	06/17/92	06/17/92	06/17/92	06/17/92	06/17/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	08/18/92	06/18/92
SAMPLE	16:00	07:45	08:30	10:30	12:30	14:30	16:30	08:55	11:55	14:55	17:55	20:55	23:55	02:55	05:55	07:55	10:02	10:15	10:24			11:07	11:23	11:27	11:30	11:55	14:02	14:13	14:22	14:40	14:49	14:56	14:58	15:00	15:02
SAMPLE	Final Eff	1:1	36	<b>E</b>	<u>26</u>	<b>6</b>	<b>E</b>	<u>.:</u>	5	<u>د.</u> 1	<u></u>	<del>ن</del>	C:1	<u>:</u>	<u></u>	<u>5</u> -	A-1 Regen	A-1 Regen			A-1 Regen		A-1 Regen		A-1 Regen		A-2 Regen	A-2 Regen						A-2 Regen	
SAMPLE	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	<b>5</b> D-1

NCEL ion Exchange Pilot Program Sample Results (mg/l)

S		1.62	2.67																				1.77	2	36.3	64.5	35.8	<b>67.4</b>							
8			2.01																				2.3	2.28											
2			0.35																				0.35	0.35											
Ž			2																				2	2											
8			2																				2	2											
ច			100.6																				96.8	96.2											
ğ			2																				2.7												
<b>5</b>																																			
8			90.2																				87.8	96.5											
2			125																				124	121											
Cd (Tot) Cd (Diss)	17.7	56.9	24.6	646	555	414	333	257	30.4	4.13	2.95	2.52	2.17	1.86	1.78	0.76	0.33	0.28	0.25	0.23	0.25	0.27	26.6	28.7	986	751	722	627	354	295	202	269	259	155	<b>6</b> 9.
ક		46.3	43.1																				<b>90.4</b>	61.0	1825	1259	1938	1675							
SAMPLING DATE	06/18/92	06/18/92	06/19/92	06/19/92	06/19/92	06/19/92	06/19/92	06/19/92	06/18/93	06/18/93	06/18/93	06/19/93	06/19/93	06/19/93	06/19/93	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/18/92	06/19/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92
SAMPLE	17:00	17:45	08:00	00:60	11:00	14:00	15:30	17:00	15:45	18:45	21:45	00:45	03:45	06:45	09:45	06:40	10:40	14:40	18:40	20:40	13:40	16:40	19:30	08:15	08:15	12:30	17:00	20:00	08:15	10:00	12:30	14:00	16:00	18:00	11:45
SAMPLE	ç.	ī	1:1	E	E	3	<b>E</b>	<b>E</b>	C-5	C-5	C-5	C-5	C-5	C-5	C-2	C-3	C-3	Ç-3	C-3	<b>c</b> .3	C-3	C-3	፤	<u>:</u>	Ö	0.0	O.O	Ö	E	<b>E</b>	8	<b>E</b>	<b>E</b>	<b>E</b>	Ç-5
SAMPLE	485	486	487	488	489	490	491	492	493	464	495	496	497	498	<b>499</b>	200	501	502	503	504	505	206	207	<b>208</b>	209	510	511	8511	512	513	514	515	516	_	<b>5</b> D-1

SS																																	9.	9.9	9	
5																																				
2																																				
\$																																				
8																																				
5																																				
8																																				
5 50																								•												
8																																				
£																																				
Cd (Tot) Cd (Diss)	2.19	2.84	3.24	4.75	5.85	8.78	7.58	0.01	988	21300	26600	15100	1930	395	110	68.9		0.2	0.17	0.5	0.17	0.5	0.14	0.17	0.16	0.17							29.5	199	582	
8																											16.8	13.9	21	17	21.7	17.9	37.1	1293	217	
SAMPLING DATE	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	08/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/50/95	06/20/92	06/20/92	06/20/92	06/20/92	06/20/92	06/22/92	06/22/92	06/22/92	
SAMPLE	14:45	17:45	20:45	23:45	02:45	05:45	08:45	14:46	15:04	15:19	15:33	15:38	15:43	15:46	15:52	15:57		09:40	12:40	15:40	18:40	21:40	00:40	03:40	05:40	08:40	10:45	12:45	14:45	16:45	18:45	20:45	00:60	00:60	12:00	
SAMPLE	C.2	C-2	C-2	C-2	C-2	C-5	C-5	C-1 Regen	C-1 Regen	C-1 Regen	C-1 Regen						•	C-3	C-3	C-3	C-3	c-3	c-3	င်းဒ	C-3	င်း	A-1	A-1	A-1	A-1	A-1	A-1	7	0.0	0.0	
SAMPLE	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	1 551	25 )-1!	ó

NCEL Ion Exchange Pilot Program Sample Results (mg/l)

Ó	111							6	13.3	<b>4</b> .8	1.29			1.68										<b>.</b>	117	281	172								
5														2.47																					
æ														0.39																					
2														2																					
8														2																					
5														8.86													2245								
8														9.1													9.7								
名																																			
8														104.2																					
2														126																					
Cd (Tot) Cd (Diss)	551													29.8	6.28	6.38	9.77	13.9	17.4	18.8	<b>19.8</b>	22.2	23.9	28.8	561	440	351	90.0	0.21	0.21	41.0	0.20	0.54	1.10	
8	1339	57.4	51.6	55.7	7.15	73.6	358	831	697	361	25.6	2.61	ო											20	820	1299	1259								90.6
SAMPLING DATE	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	08/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/22/92	06/23/92	06/23/92
SAMPLE	15:00	21:00	00:00	03:00	06:00	09:34	09:51	10:07	10:13	10:26	10:32	10:38	10:43	14:30	07:50	10:50	13:50	16:50	19:50	22:50	01:50	04:50	06:50	00:00	00:00	12:00	20:00	08:45	11:45	14:45	17:45	20:45	23:45	02:45	10:33
. SAMPLE LOCATION	0	A-1	A-1	A-1	A-1	A-1 Regen	A-1	A-1	A-1	A-1	A-1	A-1	A-1	1:1	C-5	C-5	C-2	C-2	C-2	C-2	C-2	C-2	C.2	1:1	o o	0.0	o o	C:3	C-3	C-3	C-3	C-3	င်း	C-3	A-1 Regen
SAMPLE .	553	554	555	556	557	558	623	560	561	562	563	564	565	566	267	568	869	570	571	572	573	574	675	878	577	<b>878</b>	679	280	581	582	583	584	585		1 587

NCEL Ion Exchange Pilot Program Sample Results (mg/l)

8	9.33	-	17.1	10.4	2.88	2.85														32								•								
8																				9.64																
2																				1.23																
\$																				2																
8																				2																
5	803.3	3075	1370	935	680	173														301																
8	1648	3873	6262	3414	865	194														7.8																
2																																				
8	7608	7800	17400	4800	2040	204														382.4																
ž																				416																
Cd (Tot) Cd (Diss)								6.1	2.5	7.7	9.0	<b>6</b> .	2.94	75	27	58	15	:		9.09 6.0	79	64	900	200	26600	9		32	78	0.07	ĸ.	200	22000	00	904	
3						_	_	ñ	ä	7	%	<b>∼</b>	ά	က်	Ġ.	က်	à	÷	8		Ö	લં	<b>—</b>	35	<b>5</b>	=	Ñ	ö	-	Ö	_	ē	22	à	ă	
3	594	569	587	412	156	70.3	16.9													148																
SAMPLING DATE	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/23/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	06/24/92	
SAMPLE	10:49	11:01	11:13	11:18	11:22	11:26	11:35	08:50	11:50	14:50	17:50	09:45	12:45	15:45	18:45	19:45	00:60	12:00	16:00	21:00	20:41	20:54	21:11	21:29	21:37	21:44	21:51	22:08	22:10	16:40	16:52	17:06	17:19	17:26	17:33	
SAMPLE	A-1 Regen		C-2	C-2	C-2	C-2	C-3	C-3	C-3	C-3	C-3	B	B	<b>E</b>	1:1	C-5	C-5	C-5	C-5	C-5	C-2	C-5	C.2	<b>7-5</b>	C-3 Regen											
SAMPLE	588	589	280	591	592	593	594	569	969	597	598	599	600	601	602	603	604	605	909	607	809	609	610	611	612	613	614	615	616	617	618	619	620	621	- <b>622</b>	17

NCEL Ion Exchange Pilot Program Sample Results (mg/l)

S				1.32	9.33	3	28.7	23.3	32.3	26.3	58	31.3	28.9	31.4		<b>4</b> .		34.2		32.9	32.7														16.2 2.	
8																															80	21.8	<b>5</b> 0.	22.6		
æ																																				
ž																																				
8																																				
ច				45.5	241	153	251	254	250	264	244	249	245	239		155		312		252	255														124	
Š				9.1	27	35	33	33	27	17	=	<b>-</b>	13	<b>*</b>		6.2		35		=	31														7.4	
\$5																	_																			
8																	314.4							•										•	=	
2																																				
Cd (Tot) Cd (Diss)	122	163	92.5																			59.1	2.03	<b>9</b> .	2.97	7.93	14.5	20.9	24.3	22.1	75.1	65.1	62.6	<b>88</b> .0	•	
8				56.5	121	184	271	121	203	145	123	174	176	161	212	91.9	163	156		171	187														98.5	
SAMPLING DATE	06/24/92	06/24/92	06/24/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92		06/25/92	06/25/92	06/25/92	06/25/92	08/25/92	06/25/92	06/22/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/22/92	06/25/92	
SAMPLE	17:39	17:52	17:54	08:50	09:50	10:20	11:20	12:20	15:20	18:20	21:20	00:50	03:20	07:20	08:35	09:50	10:20	11:20		13:20	16:20	08:30	11:30	14:30	17:30	20:30	23:30	02:30	06:30	07:30	06:30	11:30	15:30	18:30	13:18	
SAMPLE	C-3 Regen	C-3 Regen	C-3 Regen	A-1	A-2	A-2	A-2	A-2	A-2	A-2	A-2	C-1	<u>c.</u>	<u>-</u> -2	<u>:</u>	<u>ن</u>	<del>ن</del>	<u>.</u> .	<u>:</u>	<u>.</u> :	<b>E</b>	<b>E</b>	B	B	A-1 Regen											
SAMPLE	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	638	640	641	642	643	944	645	646	647	648	649	650	651	652	653	654	655	989	<b>29</b> 0-1	8

NCEL ton Exchange Pilot Program Sample Results (mg/l)

<b>\$</b>	52.2	215	129	136	6.69	13.2	30.8	5.79	17.5	88	181	212	149	21.4	6.21	4.68			<b>58.</b> 7																
8																																1330			
£																												0.76				<b>2</b> .0			
2																												23.4							
8																											,	13.8							
5	727.5	1060	1080	1050	908	125		32.5	97.9	595	762	1120	895	146.5	35.5	22			247									177.2							
8	556	169	1772	1566	282	58		9.5	50	1524	4944	4820	3433	82	17	<b>5</b> 6			36									106							
50																																			
8	4176	10860	14760	4920	2184	96		74.4	108	5232	17760	21120	12120	2	2	19.2			300																
2																												301							
Cd (Tot) Cd (Diss)							6.										ø,	₹.		•	5	00	00	00	92	9			.3 67.9			લ	₹.	Ξ	8
8							48.3										35	37.4		Z	6	136	235	191	1170	7	=	65	99	69	88	4	9	3.6	9.0
3	555	795	1192	604	402	72.9	210	30	70.7	429	767	865	781	89.6	22.2	160			181									70.7		103					
SAMPLING DATE	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/25/92	06/00/92	06/08/92	06/00/95	06/08/92	06/00/95	06/08/92	06/00/95	06/08/92	07/20/92	07/20/92	07/21/92	07/21/92	07/21/92	07/20/92	07/20/92	07/20/92
SAMPLE	13:31	13:43	13:52	14:04	14:10	14:17	09:45	14:30	07:48	07:59	08:15	08:30	08:42	08:47	08:54	90:60	15:15	15:45	15:45	17:07	17:21	17:37	17:54	18:02	18:09	18:15	18:29	13:50	13:50	00:00	00:90		14:40	16:40	18:40
SAMPLE	A-1 Regen		A-1 Regen			A-1 Regen		A-1 Regen	A-2 Regen	:	<u>:</u>	C-1 Regen		C-1 Regen	C-1 Regen	C-1 Regen	C-1 Regen	C-1 Regen	C-1 Regen	C-1 Regen	1:1	AC-1	1:1	AC-1	3	<u>:</u>	:	<u>5</u>							
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NCEL ion Exchange Pilot Program Sample Results (mg/l)

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NCEL Ion Exchange Pilot Program Sample Results (mg/l)

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731	C-5	11:55	07/22/92		20.5											
732	C-2	12:55	07/22/92		25.9											
733	C-2	13:55	07/22/92		30.6											
734	C-5	14:55	07/22/92		36.3											
735	C-5	15:55	07/22/92		41.3											
736	C-5	17:55	07/22/92		48.8											
737	C-2	08:30	07/23/92		58.5											
738	C-5	09:15	07/23/92		62.3											
739	C-5	10:00	07/23/92		62.4											
740	C-5	12:00	07/23/92		60.8											
741	C-5	14:00	07/23/92		59.5											
742	Filter	11:00	07/23/92		0.05											
743	C-2 Regen	15:45	07/23/92		6.31											
744	C-2 Regen	16:06	07/23/92		<b>8</b> .0											
745	C-2 Regen	16:27	07/23/92		29.7											
746	C-2 Regen	16:49	07/23/92		9650											
747	C-2 Regen	17:06	07/23/92		29600											
748	C-2 Regen	17:11	07/23/92		2560											
749	C-2 Regen	17:16	07/23/92		199											
750	C-2 Regen	17:21	07/23/92		100											
751	C-2 Regen	17:26	07/23/92		78.9											

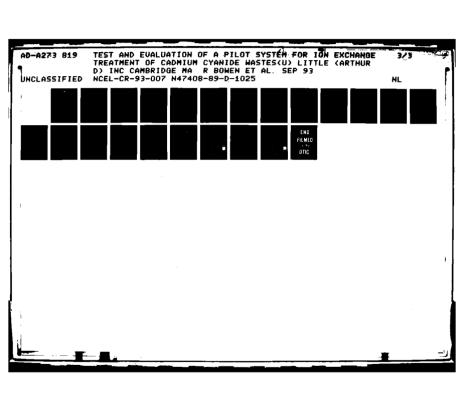
# Appendix E: Equipment List and Costs for Option No. 1

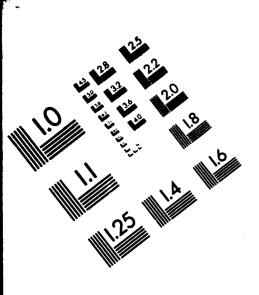
Table E-1: Equipment List and Costs for Option No. 1

item	Description	Unit Cost	No. of Units	Total Cost	Moduler Fector	installed Cost
System 100 - F	feed System					
T-101	Surge Tank, flat bottom 250 galion, HDPE	\$600	1	\$600	1.96	\$1,176
T-102	Holding Tank 750 gallon, HDPE cone-bottom with stand	\$2,900	1	<b>\$2,9</b> 00	2.55	\$7,395
F-101	In-line Strainer	\$420	1	\$420	1.21	\$508
F-102, F-103	Suspended Solids Filters, 5 micron wound filters, PVC housing	\$250	2	\$500	1.21	\$605
P-101	Transfer Pump 3 gpm, 10 psi Polypropylene wetted parts, air diaphragm pump.	<b>\$450</b>	1	\$450	3.38	\$1,521
P-102, P-103	Feed Pumps 10 gpm, 100 psi, 2HP CPVC, two-stage, flooded suction centrifugal	\$1,200	2	\$2,400	3.38	\$8,112
System 100 S	Subtotal			\$7,270		\$19,317

Table E-1: Equipment List and Costs for Option No. 1

item	Description	Unit Cost	No. of Units	Total Cost	Moduler Fector	installed Cost
System 200 -C	Cation Exchange System					
S-201	Cation Exchange Skid Three ion exchange columns operated in series, two in operation with one in standby. Each column holds 1 cu ft of resin, 1" PVC piping with automatic valves; PLC controlled regeneration. Each column is designed to be online for 5 days before regeneration.	\$35,000	1	\$35,000	2.26	\$79,100
1-202	Initial Charge of Cation Resin Amberlite IRC-718, 3 cu ft total.	\$330	3	\$990	1.1	\$1,089
System 200 S	Subtotal			\$35,990		\$80,109

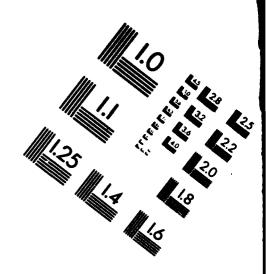


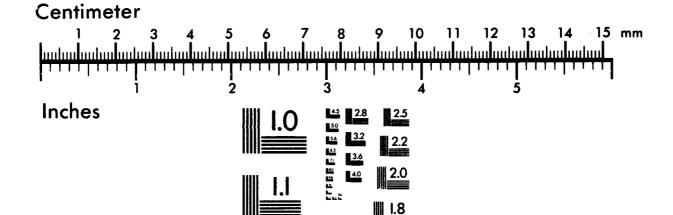


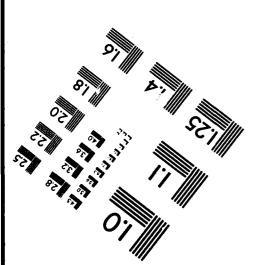


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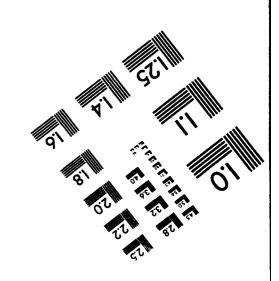


Table E-1: Equipment List and Costs for Option No. 1

ltem	Description	Unit Cost	No. of Units	Total Cost	Modular Factor	installed Cost
System 300 -	Cation Regeneration and Electr	olytic Reco	very			
T-301	Sulfuric Acid Day Tank 55 gallons, HDPE, cone bottomed with stand	\$700	1	\$700	2.55	\$1,785
T-302	Sodium Hydroxide Day Tank 55 gallons, HDPE, cone bottomed with stand	\$700	1	\$700	2.55	\$1,785
T-303	ERU Recirculation Tank 30 gallons, HDPE, rectangular with cover	\$175	1	\$175	2.55	\$446
P-301, P-302	Sulfuric Acid Metering Pump and sodium hydroxide meter- ing pump. .1-1 gpm, 50 psi, 316 SS centrifugal pump.	\$850	2	\$1,700	3.38	\$5,746
P-304	Spent sulfuric acid transfer pump. 10 gpm, 10 psi, polypropylene wetted parts, air diaphragm.	\$450	1	\$450	3.38	\$1,521
E-301, P-303	Electrolytic Recovery Unit and recirculation pump. Batch system with ERU capacity of 12.5 gallons. Open-lined vessel regulated DC power supply. Stainless steel anode and cathodes.	\$5,000	1	\$5,000	2.26	<b>\$</b> 11,300
MXR-301, MXR-302	Direct Drive Air Mixer 1/4 HP	\$700	2	\$1,400	2.55	<b>\$3</b> ,570
System 300 Si	ubtotal			\$10,125		\$26,153

Table E-1: Equipment List and Costs for Option No. 1

item System 400 - R	Description everse Osmosis (RO) System	Unit Cost	No. of Units	Total Cost	Moduler Factor	Installed Cost
T-401	RO Equalization Tank 500 gallon, HDPE, with cover, flat bottom	\$1,000	1	\$1,000	2.55	\$2,550
P-401, RO-401	Reverse Osmosis Process Unit, 1-5 gpm feed rate, 75% recovery, 90 to 95% rejection.	\$20,000	1	\$20,000	2.26	\$45,200
System 400 Su	btotei			\$21,000		\$47,750
Option No. 1 Sy	rstem - Total			\$74,385		\$173,500

# Appendix F: Equipment List and Costs for Option No. 2

Table F-1: Equipment List and Costs for Option No. 2

item	Description	Unit Cost	No. of Units	Total Cost	Moduler Fector	inst led Cost
System 100 - F	eed System					
T-101	Surge Tank, flat bottom 250 gallon, HDPE	\$600	1	\$600	1.96	\$1,176
T-102	Holding Tank 1000 gallon, HDPE cone-bottom with stand.	\$3,250	1	\$3,250	2.55	\$8,288
F-101	In-line Strainer	\$420	1	\$420	1.21	\$508
F-102, F-103	Suspended Solids Filters, 5 micron wound filters, PVC housing	\$250	2	\$500	1.21	\$605
P-101	Transfer Pump 3 gpm, 10 psi polypropylene wetted parts, air diaphragm pump.	\$450	1	\$450	3.38	\$1,521
P-102, P-103	Feed Pumps 10 gpm, 100 psi, 2HP CPVC, flooded suction, staged centrifugal pump.	\$1,200	2	\$2,400	3.38	\$8,112
System 100 S	ubtotal			\$7,620		\$20,210

Table F-1: Equipment List and Costs for Option No. 2

Item	Description	Unit Cost	No. of Units	Total Cost	Moduler Factor	Instituted Cost
System 200 -	Cation Exchange System					
S-201	Cation Exchange Skid Three ion exchange columns operated in series, two in operation with one in standby. Each column holds 2.5 cu ft of resin, 1" PVC piping with automatic valves; PLC controlled regeneration. Each column is designed to be online for 5 days before regeneration.	\$45,000	1	\$45,000	2.26	\$101,700 -
1-202	Initial Charge of Cation Resin Amberlite IRC-718, 7.5 cu ft total.	\$330	7.5	\$2,475	1.1	\$2,723
System 200	Subtotal			\$47,475		\$104,423

Table F-1: Equipment List and Costs for Option No. 2

item	Description	Unit Cost	No. of Units	Total Cost	Modular Factor	Installed Cost		
System 300 - Cation Regeneration and Electrolytic Recovery								
T-301	Sulfuric Acid Day Tank 150 gallons, HDPE cone-bottome with stand	<b>\$9</b> 50	1	<b>\$9</b> 50	2.55	\$2,423		
T-302	Sodium Hydroxide Day Tank 150 gallons, HDPE cone-bottome with stand	<b>\$9</b> 50	1	<b>\$9</b> 50	2.55	\$2,423		
T-303	ERU Recirculation Tank 50 gallons, HDPE rectangular with cover	\$250	1	\$250	2.55	\$638		
P-301, P-302	Sulfuric Acid Metering Pump and sodium hydroxide meter- ing pump. 1 gpm, 50 psi, 3/4 HP 316 SS centrifugal pump	\$850	2	\$1,700	3.38	<b>\$</b> 5,746		
P-304	Spent sulfuric acid transfer pump. 10 gpm, 10 psi, polypropylene wetted parts, air diaphragm.	\$450	1	\$450	3.38	\$1,521		
E-301, P-303	Electrolytic Recovery Unit and recirculation pump. Batch system with ERU capacity of 20 gallons. Automatic pH adjustment, open lined vessel, regulated DC power supply. Stainless steel anode and cathodes.	\$10,700	1	\$10,700	2.55	\$27,285		
MXR-301, MXR-302	Direct Drive Air Mixer 1/2 HP	\$900	2	\$1,800	2.55	\$4,590		
System 300 Su	btotal		,	\$16,800		\$44,625		
Option No. 2 S		,	\$71,895		\$170,000			

#### Appendix G - Cost Estimation Approach

### Explanation of Modular Factors for Installed Equipment Cost

Kenneth Guthrie<sup>9</sup> has developed a method for estimating capital cost purchases which utilizes a modular factor to account for indirect costs in addition to the capital purchase price of a unit piece of equipment. We have used Guthrie's Chemical Process Module to estimate modular factors for the ion exchange equipment. Guthrie provides published modular factors for some specific equipment, whereas some modular factors were estimated.

Figure G-1 is an illustration of Guthrie's Chemical Process Module. This illustration assumes an equipment capital investment of \$100,000. One can use a combination of the illustrated factors to arrive at the total module cost. Included in the factors are such items as materials, labor, electrical, instrumentation, steel, piping, concrete, insulation, paint, and field installation. An explanation of the various factors is provided below.

Material Factor: Indicates the relationship between the capital equipment cost and total field materials associated with the equipment. The material factor generally ranges from 1.42 to 1.75.

Labor Factor: This includes all field labor required to install the equipment and erect the field materials. It generally ranges from 0.54 to 0.66. This does not include fringe benefits or labor burdens, which are included in the overhead account.

L/M Ratio: Relates direct labor to direct material. It is an important measure of productivity and ranges from 0.32 to 0.4.

Direct Cost Factor (M&L): Relates equipment capital cost to the dost of the equipment together with cost of field materials and field labor necessary to install the equipment on a prepared job site. Ranges from 1.8 to 2.6.

Indirect Cost Factor: Includes indirect cost elements associated with the module or project. This factor is sensitive to materials of construction, labor productivity, field supervision, site location, and dollar magnitude. The average value is 1.34 to 1.38.

Bare Module Factor: This include all direct and indirect cost elements in the process module, and is used as a multiplier on the equipment cost. It is a measure of the cost required to integrate single or multiple pieces of equipment into a system. This factor ranges from 2.38 to 3.64.

Total Module Factor: Includes all estimated costs in the bare module plus any contingencies considered necessary to adjust for unlisted items or due to the lack of sufficient detailed design information as well as contractor fee. The contingency used ranges from 18 to 30%.

#### **Development of Modular Factors**

The modular factors shown in Appendix E and F are Total Module Factors. The following is an explanation of the source of these modular factors.

#### Pumps:

Pumps require electrical or pneumatic power, instrumentation such as pressure gauges and level controls, piping connections, and mounting. These costs are taken into account by the modular factor outlined by Guthrie. A module factor of 3.38 is estimated which includes piping, concrete, instruments, electrical, insulation, and paint the factor also included field labor, material erection, freight, insurance, and taxes. No contingency was added to this factor due to the simplicity of the installation.

#### Tanks:

Again, a factor taken from Guthrie was used for installed tank cost. For cone-bottomed tanks a bare module factor of 1.96 was used with a contingency of 30%, resulting in a total module factor of 2.55. All flat bottom tanks were assumed to have no contingency and had a total module factor of 1.96. Tank installation includes setup labor and piping.

#### Mixers:

Guthrie<sup>8</sup> provides Field Installation Factors for specific pieces of equipment. Propeller mixers are estimated to have a field installation factor of 1.38. If it is assumed that the indirect factor is 1.38 and an additional 30% contingency is added, the total module factor is equal to:  $1.38 \times 1.38 \times 1.3 = 2.5$ .

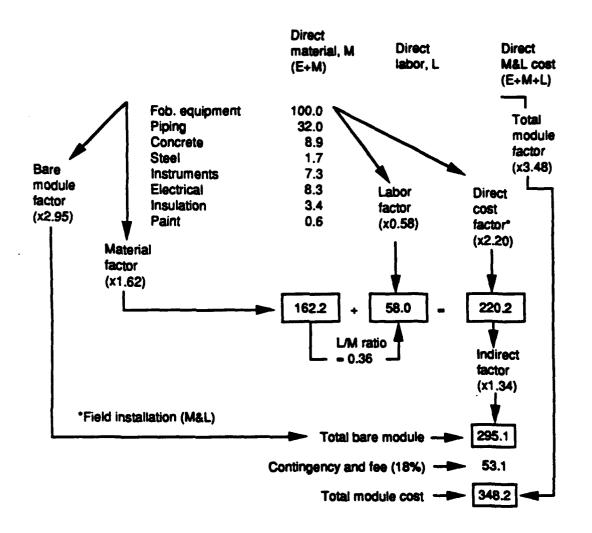
#### Other:

The total module factors for the other equipment modules were estimated. These include the following:

Equipment	Total Module Facto
In-line Strainer	1.21
Suspended Solids Filter	1.21
Initial Charge of Resin	1.1
Ion Exchange Skid	2.26
<b>Electrolytic Recovery System</b>	n 2.26
Reverse Osmosis System	2.26

The in-line strainer, suspended solids filter, and resin charge all have very low modular factors. This is due to the simplicity of the installation, the minimum amount of labor required, and the possibility that the modular factors for the other major pieces of equipment already have some piping and installation labor built in which may include these auxiliary pieces of equipment. The ion exchange skid, the electrolytic recovery system, and the RO system also have estimated modular factors. Again, the factors are less than those for tanks and pumps because they are assumed to be skid-mounted systems with little installation labor required. Some labor is required for instrumentation, rigging, pipe connections, and power.

Figure G-1: Chemical Process Module



Source: Guthrie, K. M., Chemical Engineering, March 24, 1969.

# Appendix H: Water Balance and Chemical Consumption Calculations

## **Appendix H - Calculations**

#### **Water Balance**

## Option No. 1 (with RO Treatment)

Rinsewater and chemical requirements for regeneration:

Regen Step	Holding Tank	ERU Tank	NaOH Tank	IWTP	Total (gals)
Initial Rinse	60				60
Acid Regen	8	5			13
Slow Rinse		8		14	22
Fast Rinse				105	105
NaOH Neut.			7	8	15
Final Rinse			8	97	105
Totals	68	13	15	224	

224 gallons to IWTP every five days from regen 224/5 = 44.8 gallons per day (gpd)

Total rinsewater use = 60 + 22 + 105 + 105 = 292 gals 292 gals/ 5 days = 58.4 gpd

Assume 25 gallons per day lost to evaporation and dragout. Assume RO receives 1000 gpd rinsewater + recycle to hold tank= 1000 + 136/5 = 1014 gpd

Assume 75% Flow recovery in RO (1000 + 14) x 75% = 760 gpd Recycled (1000 + 14) x 25% = 253 gpd to IWTP

Total makeup required in rinse tank = 1000 + 25 - 760 = 265 gpd

Total Discharge to IWTP = 44.8 gpd + 253 gpd = 298 gpd

Total water use = 265 + 58.4 = 323 gpd x 365 days/year x 1 1000 gallons/1000 gallons = 118 1000 gallons per year water use

### Option No. 2 (without RO Treatment)

Assume 1000 gpd of rinsewater required.

## Rinsewater and chemical requirements for regeneration:

Regen Step	Holding Tank	ERU Tank	NaOH Tank	IWTP	Total (gals)
Initial Rinse	150				150
Acid Regen	20	12			32
Slow Rinse		20		36	36
Fast Rinse				262	262
NaOH Neut.			19	18	37
Final Rinse			12	250	262
Totals	170	32	31	566	

566 gallons to IWTP every five days from regen 566/5 = 113.2 gallons per day (gpd)

Total rinsewater use = 150 + 56 + 262 + 262 = 730 gals 730 gals/ 5 days = 146 gpd

Assume 25 gallons per day lost to evaporation and dragout. Assume cation exchanger receives 1000 gpd rinsewater + recycle to hold tank= 1000 + 170/5 = 1034 gpd

Total makeup required in rinse tank = 1000 + 25 = 1025 gpd

Total Discharge to IWTP = 113 gpd + 1034 gpd = 1147 gpd

Total water use = 1025 + 146 = 1147 gpd x 365 days/year x 1 1000 gallons/1000 gallons = 419 1000 gallons per year water use

## **Chemical Consumption**

**Options No. 1** 

Acid Regeneration: 13 gallons 10% H2SO4 required per regeneration

73 regens /year x 13 gallons / regen = 950 gallons per year 10% H2SO4

Assume lose 10% to bleed stream = 95 gallons per year

Assume 70% of the remaining is reused = 600 gallons per year

950 gallons required - 600 gallons recycled = 350 gallons per year of 10% acid required to be purchased

Need 3.1 gallons of 98% H2SO4 for every 50 gallons to make a 10% solution.

= 22 gallons of 98% acid per year

Use 25 gallons

NaOH Neutralization: 15 gallons 5% NaOH required per regeneration

1 regen / 5 days x 73 regens / year x 15 gallons / regen = 1095 gallors per year of 5% NaOH

Assume lose 10% to bleed stream = 110 gallons per year

Assume 70% of the remaining is reused = 690 gallons per year

1095 gallons required - 690 gallons recycled = 405 gallons per year of 5% NaOH required to be purchased

Need 7.3 gallons of 50% NaOH for every 100 gallons of water

= 30 gallons of 50% NaOH per year

Use 35 gallons

#### **Chemical Consumption**

Options No. 2 (Without RO System)

Acid Regeneration: 32 gallons 10% H2SO4 required per regeneration

73 regens /year x 32 gallons / regen = 2336 gallons per year 10% H2SO4

Assume lose 10% to bleed stream = 234 gallons per year

Assume 70% of the remaining is reused = 1471 gallons per year

2336 gallons required - 1471 gallons recycled = 865 gallons per year of 10% acid required to be purchased

Need 3.1 gallons of 98% H2SO4 for every 50 gallons to make a 10% solution.

= 54 gallons of 98% acid per year

Use 60 gallons

NaOH Neutralization: 38 gallons 5% NaOH required per regeneration

1 regen / 5 days x 73 regens / year x 38 gallons / regen = 2774 gallons per year of 5% NaOH

Assume lose 10% to bleed stream = 277 gallons per year

Assume 70% of the remaining is reused = 1748 gallons per year

2774 gallons required - 1748 gallons recycled = 1026 gallons per year of 5% NaOH required to be purchased

Need 7.3 gallons of 50% NaOH for every 100 gallons of water

= 75 gallons of 50% NaOH per year

Use 80 gallons

# **Cadmium Recovery**

1000 gpd at 30 mg/L Cd

 $1000 \text{ gpd} = 3785 \text{ L} \times 30 \text{ mg/L}$ 

- = 114 grams/day Cd x 365 days/year
- = 41,145 grams/year x 1lb/454 grams
- = 91 lbs/year Cd recovered

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